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College of Natural and Computational Sciences

Department of Chemistry

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Spectroscopic Studies on Natural Gem Opal Hosted in Ethiopia: South Gondar

By

Woldesenbet Bafe Dilebo

Advisor: Walelign Wubet Melkamu (PhD)

Co-advisor: Kumlachew Zelalem Walle (M.Sc.)

A Thesis Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science in Chemistry (Inorganic)

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Thesis Approval Sheet

The thesis entitled “Spectroscopic Studies on Natural Gem Opal Hosted in Ethiopia: South Gondar” by Mr. Woldesenbet Bafe Dilebo is approved for the degree of “Master of Science in Chemistry (Inorganic)”.

Examiners

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Woldesenbet Bafe

June, 2017

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List of Acronym

CT	Cristobalite, Tridymite
FAAS	Flame Atomic Absorption Spectroscopic
IR	Infrared
Opal-A	Opal- Amorphous
Opal-AG	Opal- Amorphous-Gel
Opal-AN	Opal-Amorphous, Network
POC	Play Of Color
RI	Refractive Index
SG	Specific Gravity
SEM	Scanning Electron Microscope
TEOS	Tetraethyl orthosilicate
USD	United State Dollar
UV	Ultraviolet
XRD	X-Ray Diffraction

Abstract

SPECTROSCOPIC STUDIES ON NATURAL GEM OPAL HOSTED IN ETHIOPIA: SOUTH GONDAR

The representative sample of gem-opal was collected from south Gondar mines and energy bureau. This sample was identified and characterized by different physical property measuring devices and advanced spectroscopic techniques. In order to verify that the sample was indeed opal a refractometer, heavy liquid method and "MOHS HARDNESS PENCILS" were used. The performed physical analysis shows that the hardness value is between 5.5- 6; the refractive index value is in the range between 1.437-1.445 and the specific gravity value is between 2.02-2.3; the measured values are comparable with literature data which verify that the samples were indeed opal. The contents of trace elements; (Mg, Cu, Mn, Ca, Fe and Zn) were analyzed by Flame Atomic Absorption Spectroscopy (FAAS) technique. The metal level observed in investigated sample is comparable with their corresponding worldwide report values. It is observed that the intensity of the orange color (from yellow to orange to red to "chocolate"-brown) correlates with the large amount of iron concentration and white color correlate for large amount of calcium concentration. The appearance of the light brown color on a sample is associated with small contents of Mn and blue color is associated with the presence of Cu, Mg and Zn silicate inclusion. The characteristic FTIR and XRD spectra data have significant contribution for the identification and characterization of the investigated sample. The FT-IR spectra analysis was characterized by spectra features of molecular water and silanol (Si-OH) groups, in which broad absorption bands centered around 3460 cm^{-1}, due to the O-H stretching vibration of water molecules and water bending vibration occur around between 1640 cm^{-1}-1625 cm^{-1}. In the low frequency region from 2000 cm^{-1}-500 $cm^{-1}$the sample has three bands centered around 520 cm^{-1}, 800 cm^{-1} and 1020 cm^{-1}, these bands are due to the absorption of silicate(Si-O) frame work vibration. The performed XRD analysis show that the sample has five resolved peaks around 20.65°, 21.8°, 36.05°, 44.5° and 56.85° and has two weak peaks at ~28.5° and ~31.4° with 2Θ values between 10° to 70°. The five resolved peaks and the two weak peaks are characteristic peak positions for opal-CT and opal-C opaline minerals respectively. The results are comparable to literature data.

***Key words*:** *Gemstone; Gem-opal; FTIR; XRD Spectroscopy; FAAS; Ethiopia*

1. INTRODUCTION

1.1. Background of the study

A mineral is a naturally occurring inorganic element or compound having an orderly internal structure and characteristic chemical composition, crystal form, and physical properties. Minerals differ from rocks, which are naturally occurring solids composed of one or more minerals. Rocks do not have a distinctive chemical composition or crystal structure**.** Ethiopia is endowed with rich mineral resources and offers excellent opportunities for mineral prospecting and development. Geological studies have identified a favorable geological environment hosting a wide variety of mineral resource. According to the Ministry of Mines and Energy, Ethiopia, the biggest developed mine in the country is that of southern Ethiopia's Lega Dembi gold mine. It is the largest gold mine in the country with total estimated reserve of 82 tons and average annual production of 3.6 tons. Additional reserves are expected to be identified in at least seven regions of the country [1]. In addition to gold, there are good deposits of tantalum, platinum, nickel, potash and soda ash. Among construction and industrial minerals are marble, granite, limestone, clay, gypsum, gemstone, iron ore, coal, copper, silica, diatomite, etc. Geothermal energy also exists in good quantity.

The gemstone exploration has recent history in Ethiopia. There are few studies on Ethiopian gemstones conducted by different researchers. The diverse geology of Ethiopia comprises a Varity of metallic, precious gemstone and industrial mineral [2]. Gemological finding indicates that many parts of Ethiopia are potential sources of precious and semi precious stones. Studies have so far shown that the following gemstones are found in Ethiopia: Emerald, Apatite, Almadine, Amethyst, Aquamarine, Chalcedony, Citrine, Jasper, Peridot, Topaz, Diamond, Sapphire, Tourmaline and opal.

Opal is found in Afar region, Northern Shewa, Wello and Gondar suggesting that it is a huge belt extending from Eastern to central Ethiopia. The occurrence of precious opal reported in Warder, Ogaden and Dire-Dawa. The precious opal has become an important mineral commodity, because it has satisfactory structural stability, durability, play of color, color saturation and color patterns. Due to these demands, precious opal has become an important mineral. Current price of rough, cut and polished gem-quality Opal is $1450-1600 USD per kilograms [3]. Ethiopian opals

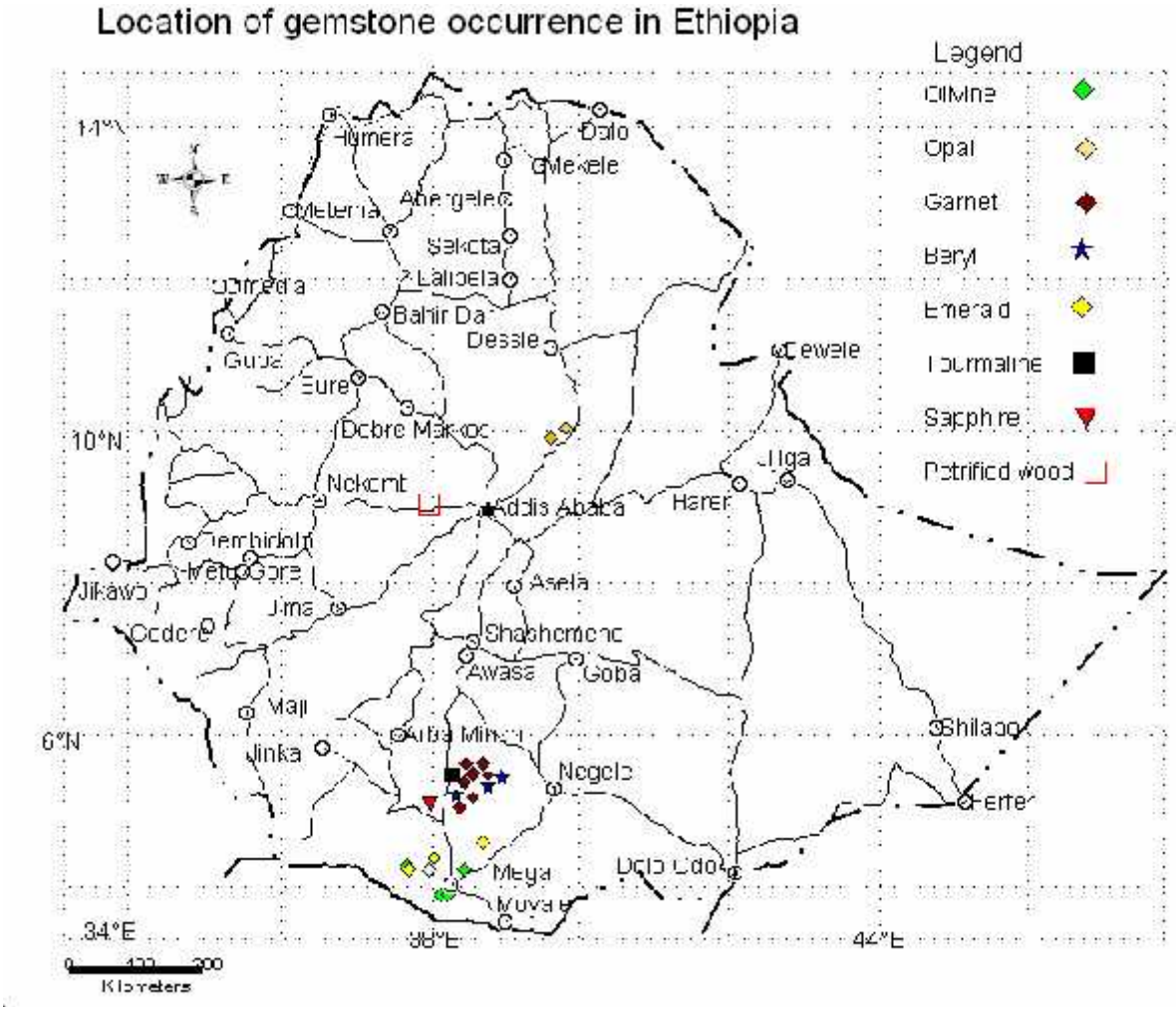


Fig. 1. Location of gemstone occurrence in Ethiopia [3]

take “the gem world by storm” in their quality. For a while now, numerous jewelry auctioneers and dealers' web pages have been displaying the most beautiful opals from Ethiopia to the international market. Some even considered them threats to Australia's huge and equally beautiful opals. In fact, lately on the news of "the amount of Ethiopian opal offered for sale increasing dramatically in the opal market," an Australian in opal business in 2010 wrote," At the possible wrath of some Aussie opal lovers I dare to make this statement. If this field is as extensive as it may well be, perhaps in the future, Australia could lose its dominance in the light opal market.”

Given the diverse geology of Ethiopia, this could only be the curtain-raiser for what is to come, provided that the country uses its resources properly and for the benefit of all its citizens. In other words, there could still be more areas burying these semi-precious stones of amazing varieties Ethiopia has yet to uncover and make use of them to the benefit of its citizens. By

now, the world already has a taste of the Ethiopian opals. And the little that has so far been known of them, especially their brilliant qualities and abundant “play of color[s]”, have proved irresistible attractions [4].

Therefore, mining operations of gem-opal within the country is expected to be an important economic catalyst for the Government’s export-orientated development strategy. By recognizing the need to promote the market-oriented modern mineral production, processing and marketing system, the Ministry of Mines established Mineral Market and Value Chain Development Directorate in 2014 bestowed with diverse responsibilities. In 2013, gemstone exports were 25,078 kg and opal accounted for 98% of gemstone exports by value. Almost all gemstone mines are dominated by artisanal, low-tech mining system. Miners are collecting and selling of rough gem to local market. Currently, almost all of the gemstones of our countries are exported as rough. Therefore the government have to work to improve policy, legal and regulatory frameworks of the sector, improving the working systems and expand the geo-sciences mapping coverage of the country both in quality and accessibility [5, 6].

Now a day a variety of treated and synthetic gem materials are encountered today in the jewelry marketplace in increasing their quantities. Although it is normally entering into the market with correct information, in some cases this material are sold with incorrect or inaccurate information on their identity. Hence the introduction of this synthetic and simulated opal gemstone on the gem market led to its destabilization and loss of customer confidence. This is particularly observed in the jewellery market. Therefore, advanced spectroscopic technique is important to determine and characterize this natural and synthetic gem-opal.

The physical and chemical features can be related to the gemological properties of the opals, like the body color or the luminance and also the process of formation and the area of provenance. Therefore identification of chemical and physical properties of opals from a particular geographical location is important for several reasons. For example, for the sellers are very useful to know the provenance, as the gems of some localities are more valuable than others. In addition, in the knowledge of the geographical origin is crucial to reconstruct the trade routes of gem [7].

This paper presents results of the physical properties such as refractive index, specific gravity, and hardness as well as the spectroscopic techniques such as FT-IR, XRD and AAS that were used to identify and characterize the natural gem-opal hosted in Ethiopia, South Gondar. This

study may be helpful for discrimination between natural opals hosted in Ethiopia with the other natural opals studied by different researchers in different countries (such as Australia, Mexico, Macedonia, USA, etc.) for the gem trade south Gondar.

1.2. Chemistry of Opal

1.2.1. Formation and occurrence

The word natural opal derived from a word Sanskrit in Latin it means “jewel stone”. Opal is an amorphous form of silica, (SiO_2-n-H_2O), containing 3% to 21% water within the mineral structure and it has been favored for many centuries. It is very fragile and is damaged quite easily but it is beautiful. Natural opal is one of the most known and expensive gemstones. Its beauty depends on optical properties. Natural opal consists of nanosized marbles of SiO_2 and the pores between the marbles are filled with amorphous glass. Their intensity of light diffracted by a crystal is defined by optical property of spheres (marbles) and pores. However, gem-opals have weak contrast of index of refraction between SiO_2 spheres and pores and it consists of many different micro crystals [8].

1.2.2. Formation from Water near the Earth Surface

A number of models have been proposed to explain the origins of the formation of such an interesting natural structure. The models take on a number of forms, but all need a supply of silica for the formation of the opal. In sedimentary environments, the silica is most likely to be derived from the sandstones by chemical weathering of relatively soluble silicates such as the feldspars contained in the sediments. Using typical potassium feldspar as an example, the chemical weathering occurs by dissolution of the feldspar. During the weathering process, feldspathic tuffs are readily kaolinzed and converted to soft earthy masses formalized in eq. (1)

$$\mathbf{2KAlSi_3O_8 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2KOH + 4SiO_2 \ldots\ldots \text{Equ. 1.}}$$

Note that this reaction also involves hydration as well as the dissolution of K^+. In this reaction, Al and many similar hydrolysis reactions may be released as well-crystallized clay mineral or as colloidal, Aluminosilcate and SiO_2 as colloidal silica, or solid quartz, opal or other silica mineral.

The sorption may be occur with released cation to the surface of colloidal particles or released to solution. These adsorbed ions are then available for reaction and exchange with the passing

solution. Although hydrolysis can take place in pure water, the reaction is intensified in the presence of natural acids, of which the most common are carbonic acid [9].

The permeation of ground water through the sediments resulting in kaolinite and dissolved silica, aided by an increase in P^H (8-10) through the release of potassium hydroxide. If the silica is in solution, the enrichment of the solution can occur by evaporation. An increase in the concentration of the silica solution coupled with a lowering of the P^H through alkali ion exchange with the surrounding clays allow the nucleation of primary silica spheres and subsequent sphere growth as more is supplied to the system [10].

Also relative small amount of dissolved carbon dioxide or carbonic acid which are contained by rain water, enough to weather feldspars and dissolved great quantities of rock over a long time. The full balanced form of the weathering reaction can be written as:

Feldspar + Carbonic acid + Water → Dissolved Kaolinite +Silica+ Potassium

$2KAlSi_3O_8 + 2H_2CO_3 + H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2K^+$ ..... Equ. 2.

This simple weathering reaction illustrates the three main chemical effects of chemical weathering on silicates. This can be leaches, or away cations and silica. And also it hydrates, or adds water to the minerals; therefore, it makes the solutions less acidic. Specially carbonic acid in rain water helps to weather in different way such as small portion of carbonic acid molecules ionizes, forming hydrogen ions (H^+) and bicarbonate ions (HCO_3^-) and thus making the water droplet slightly acidic; and the slightly acidic water dissolves potassium ions and silica from feldspar, this leaving a residue of kaolinite (solid clay); the hydrogen ions from the acid combine with the oxygen's of the feldspar to form the water in the kaolinite structure; the kaolinite becomes part of the soil or is carried away as a sediment; the solution becomes less acidic as the reaction goes on; the dissolved silica, potassium ions (K^+) , and bicarbonate ions are carried away by rain and river waters and ultimately are transported to the ocean. Then after, opal is formed from a solution of silicon dioxide and water.

As surface or ground water move through the earth in response to hydraulic or topographic gradient, it picks up silica from the products of the weathering reaction(solution), and carries this silica rich solution in the cracks and voids, therefore primary and secondary openings, veins, caused by natural faults, fractures, decomposing fossils and other silica deposit. This cycle repeats over very long period of time, and eventually opal is formed [9].

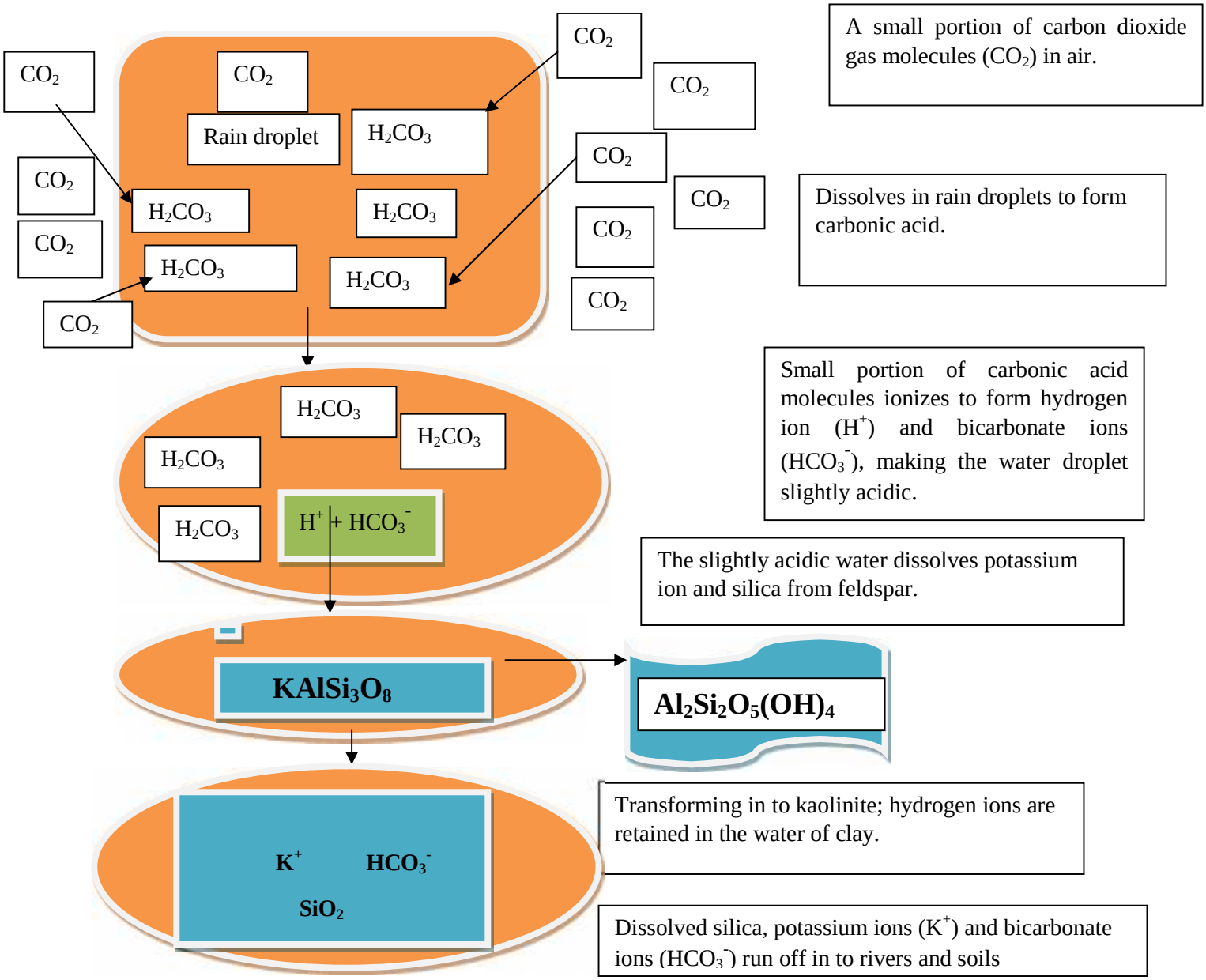


Fig. 2. Feldspar weathering when it is in contact with carbonic acid from rain water containing carbon dioxide. Two products are formed: kaolinite clay and a solution containing dissolved silica, potassium ions, and bicarbonate ions [9].

It is generally accepted that opaline silica is formed by precipitation from aqueous solution. This precipitation was followed annealing process, either by thermally or pressure induced methods. Initially the opal is precipitated into opal-A form and then annealed into the other form with time. The mechanism of precipitation is most likely to be initially associated with formation of colloidal silica particle with nanometer dimensions [11].

Under favorable conditions, spheres of silica, contained in silica rich solution in the earth are formed and settle under gravity in void to form layers of silica spheres. Silica spheres of uniform size may be formed through the process, therefore, precious opal commences to form. For precious opal, the sphere size is approximately from 150 to 400 nanometers. This type of opal can show a play of color in the visible light range of 400 to 700 nanometers [9].

Opal is made of closely packed spheres of silica in hexagonal and /or cubic closets packing. The void between the spheres is occupied by air and water. In common opal the domains of equal spheres with uniform packing are small and non-existent whereas in precious opal, large domains are made up of regularly packed spheres of the same size. Variable interplay of internal color is the characteristic of Precious opal [12]. Depending on the method of formation, the diameter of the spheres can vary in the range between 100-500 nm [13].

Precious opal composed of silica spheres at micro scales level from some 150 to 300 nm in diameter in a hexagonal or cubic close-packed lattice. The internal colors are produced by ordered silica sphere, these causing the interference and diffraction of light passing through the microstructure of gem-opal. The quality of precious opal can be determined by the regularity of the size and the packing of these spheres. Approximately half of the wave length of a component of visible light is the distance between the regularly packed planes of the spheres. And the light of that wave length may be subject to diffraction from the grating created by the stacked planes. The spacing between the planes and the orientation of planes with respect to the incident light determines the colors observed [12].

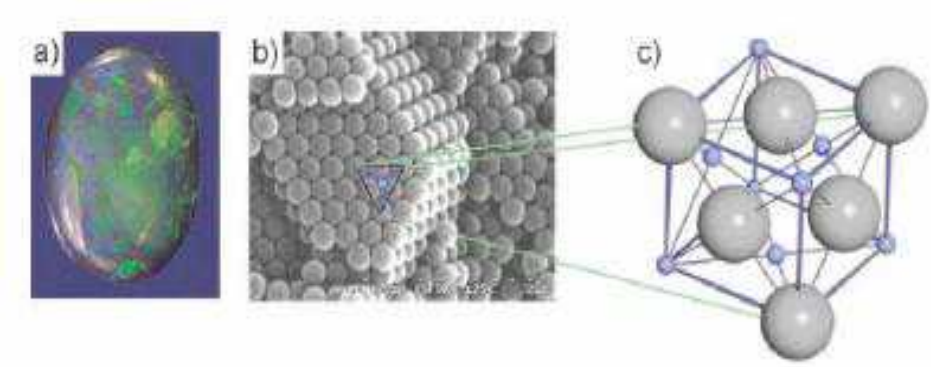


Fig. 3. (a) natural opals (b) SEM image of the opal nanostructure, which is responsible for the color effects by interference; c) the face centered cubic (fcc) lattice used for the description of the nanostructure lattice [14].

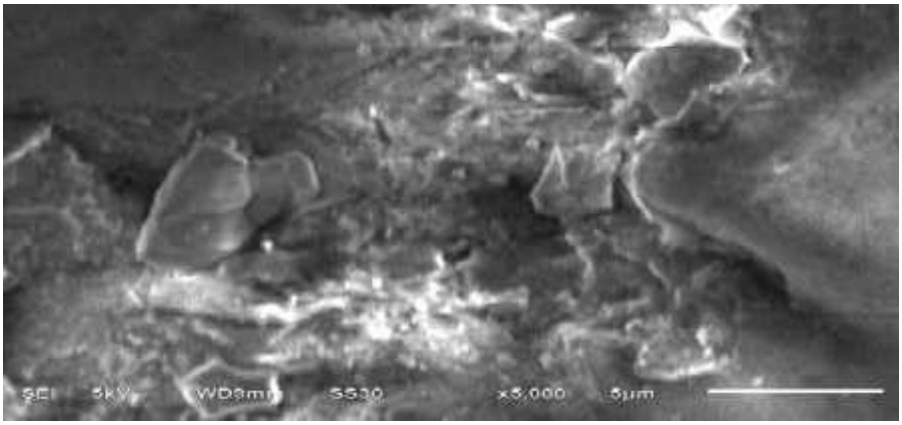


Fig. 4. Representative SEM image of natural common opal [15].

Opal is one of the planets rarest and unique gemstone which is found in some places. Opals have unique patterns that no one else in the world owns. The unique patterns that make it differ from other gem types are their characteristic color depth, shade and the play of pattern [16]. They are found in different parts of the world.

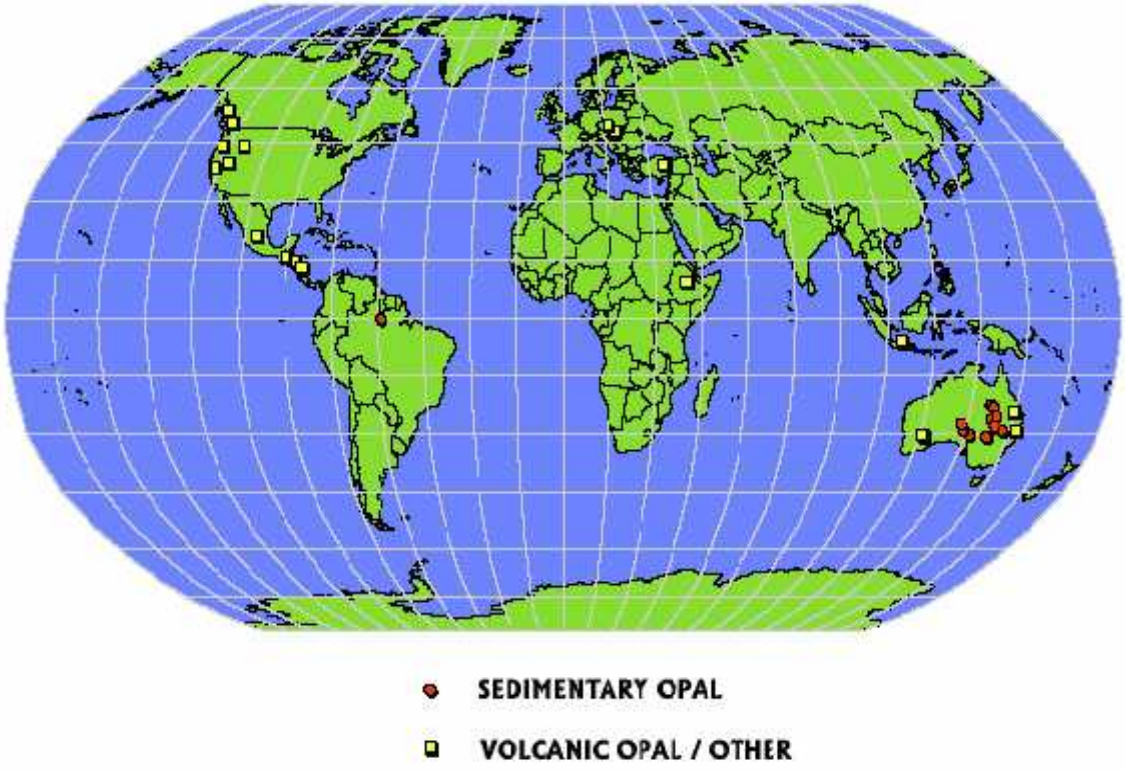


Fig.5. Precious opal deposits of the world [17].

Australia produces the largest variety of opal in the world. Opal can also be purchased from Ethiopia, Mexico and Honduras and all have their own color and pattern attributes. No other

stone can match opal. This uniqueness of owning a stone that no else is the advantage of opals [16].

Fig. 6. The different types of opal in the world [16].

Opals of the world have been our most popular download for opal posters. People enjoy the natural colors and appealing aspect of the design, shapes and pattern on these opals. The opals displayed in the above image include; Black Opals from Australia, Australian Cooper Pedy Opal, Australian Andamooka Opal, Australian Koroit Opal, Australian Yowah Opal, Australian Mintabie Crystal Opal, Australian Boulder Opal, Brazilian Opal, Ethiopian Welo Opal, Honduran Opal and Mexican Opal [16].

1.3. Types of opals

There are so many type of Opal in the market that it can sometimes be overwhelming to try to identify them all.

Solid opals: refers to the type of opal where the entirety of the gemstone is natural and no additional layer(s) of material have been attached to the opal layer. These opals are the most valuable and it can be cut into a solid piece [18].

Fire opal: Is a type's opal from Mexico which has reddish or orange color but does not show play of color.

Boulder opal: Results from splitting of a seam of opal running the rock or boulder. The polished piece will have opal as its face and the rock material as its base.

White opal: Are white base, more common variety of opals that are usually the least expensive.

Black opal: Is rarer than white and warrant's a higher price.

Semi-black opals: Are opals with base colors from medium gray to dark gray. Gray opals have a base color of medium to lighter gray color.

Crystal Opal is transparent enough to see through them. Various colors and fire can be seen as light rolls through them [19].

Based on Crystallinity, opal can be classified in to two.

I. Microcrystalline opal

II. Non-crystalline opal

1.3.1. Microcrystalline opal

It consists of opal-CT (tridymite) and opal-C (cristobalite). Opal-CT has been interpreted as consisting of clusters of stacking of cristobalite and tridymite over very short length scales. A microcrystalline blade of cristobalite and tridymite are used to prepare the sphere of opal-CT. Thus opal-CT has contained high water as 10 wt% [20].

1.3.2. Noncrystalline opal

This consists of different types of opal, like opal-A, opal-AN and opal-AG. Opal-A is a biogenic form of silica, opal-AN (“hyalite”) is a hydrous amorphous silica glass. Two broad categories of noncrystalline opals, some time just referred to as "opal-A", have been proposed. The first of these is opal-AG consisting of aggregated spheres of silica, with water filling the space in between [8, 20].

Based on x-ray diffraction (XRD) measurements, opaline silica is divided into three categories: opal-C (relatively well ordered α-cristobalite), opal-CT (disordered α- cristobalite with α-tridymite-type stacking), and opal-A (amorphous) [21]. The deposition of opal is common in both volcanic and sedimentary rocks as primary and secondary phase. The term opal-A (amorphous) is used for nanocrystalline opal structures or commonly called sedimentary opals that lack sharp peaks, and give a hump at between approximately $2\Theta = 20\text{-}30^{\circ}$ in their XRD patterns [22].

A play-of-color phenomenon caused by visible light diffraction on the stacking and whether it is transparent and vividly colored are important to classify as precious and common, or halite (semi precious) under gemological properties. Precious opals are mostly known by either

sedimentary opaque, translucent-black and volcanic transparent-translucent fire or white opal. However, the common or hyalite opals have the more varied origins. They occur as sedimentary or volcanic rocks and are almost entirely opaque. Their appearance and colors are caused by their absorbance and by the inclusion of some metal transition trace elements [23].

In Ethiopia precious opal is found in tertiary volcanic with in rhyolitic ignimbrite or tuff as concretions that are covered by compacted acidic ash shell with different colored amorphous silica in center. The opal have generally large size and wide range of colors, including clear, translucent, white, yellow, orange, red, blue, green and dark reddish brown [14].

A macroscopic and geological picture indicated that amorphous silica cement is very abundant in deeply weathered profiles in which precious opal are found [24].

1.4. Valuing Opal – the value of opal

The values of opal can depends on many factor such as body tone, brilliance, pattern, color bar thickness, faults and the play of color are very important in determining and characterizing the value. Other important factors are including the quality of the cut, polish and size of the stone.

Body tone: This is the most important factor in classification and valuation of opal. Body tone refers to the background or the underlying color of the opal which ranges from black through dark to light. Generally, opals with a black or dark body tone are more valuable than those with a white, light or crystal body tone.

Brilliance: the brightness and clarity of the color displayed by opal is describing brilliance properties, when the stone is viewed face-up. The brilliance range is from brilliant bright to subdued or dull.

Pattern: The regular arrangement of colored segments, forming the play of color of a precious opal is unique to every individual opal. The distinctiveness and color displayed by this segment determines the quality of the pattern of opal.

Color Bar: The thickness of the color bar in opal is relative to the overall size and shape of the individual stone. Boulder opal typically has a very thin color bar due to the way the opal is geologically formed.

Play of color:- the diffraction of white light by the internal structure of orderly arrayed spheres of silica are causing the brilliant range of the full spectrum of colors these phenomenon known as the play of color.

Faults: – Various faults can detract the value of a finished opal. A crack in the face can render almost worthless an opal. Crazing, i.e. many small cracks in the opal's face will relegate the stone to worthless [19].

1.5. General physical Properties of opal

They have different physical and chemical properties for opal gemstone. Having a broad knowledge about the most important properties of opal gemstone are able to measure the value to the opal gemstone cutter and setters as well as to the wearer of the jewelry and the collector [25]. There are a limited number of elements and chemical compounds used to determine their physical characteristics of gemstone. The most important physical characteristics that are generally accepted are hardness, refractive index, specific gravity and color, although thermal stability, chemical stability and toughness are also considered important in many gemstone applications [26].

1.5.1. Hardness

The word hardness in case of mineral and gemstone refers to scratch hardness or cutting resistance. Scratch hardness defined as the resistance of mineral when scratched with a pointed testing object. The hardness values are measured by Mohs' scale. Gemstone of the scratch hardness (Mohs') 1 and 2 are considered as soft, those of the degrees 3 or 5 are medium and those over 6 are hard. The hardness values of precious opal range from 5.5-6.5. These scratch hardness test played a large role for the determination of gemstone [25].

1.5.2. Specific gravity

Specific gravity (SI) or the relative density of a gem material is important to gemologists in identifying an unknown specimen, and to jewelers and jewelry lovers in matching the setting size to the gem weight. Specific gravity is calculated as the ratio of the density of a given volume of the gem to the same volume of water. In general specific gravity is determined by a gem which have heavy elements in their chemical formulas, like lead or iron, and those which crystal structures pack the atoms tightly, have high specific gravity while those made of lighter elements or those with loosely packed crystals have low specific gravity. Therefore gem-opal has specific gravity value between 2.01-2.2 [25, 26].

1.5.3. Color

Color is the most important characteristic of gems. In cause of most stone it is not diagnostic in identification, because many have the same color and numerous stone occur in different colors [25]. The color of opal shows a magnificent feature. Opals can display all color of the rainbow in an iridescent, moving pattern of red, green, blue, yellow, purple, aqua, pink and any other color you can imagine. The pattern and arrangement of the color, which is displayed in an opal, can take on many beautiful forms, and the movement of color across the face of a stone is known as the play of color. A series of colors as the angle of the incident light changes are produced by the interference of light either at the surface or in the interior of a mineral. The striking flashes of varied color against a white or black background, as seen in precious opal, are called play of colors (POC) [27]. In addition, it spans a range from colorless, white, brownish-white, yellowish-white, yellowish to greenish white to grayish [28].

The color of gemstone can be caused by metal and their combinations, especially chrome, iron, cobalt, copper, manganese and vanadium absorb a certain wavelength of light and so case coloration. The opal spans a range from colorless, white, brownish-white, yellowish-white, yellowish to greenish white to grayish [29]. The color of precious opal is caused by impurities of different transition metal element. For example the blue color has been shown to be resulted from the intervalence charge transfer, namely the transfer of electrons from Fe to the Ti in adjacent sites.

$$Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+} \text{..... Equ. 3}$$

This process involves absorption of yellow light resulting in transmission of the complementary blue color [19].

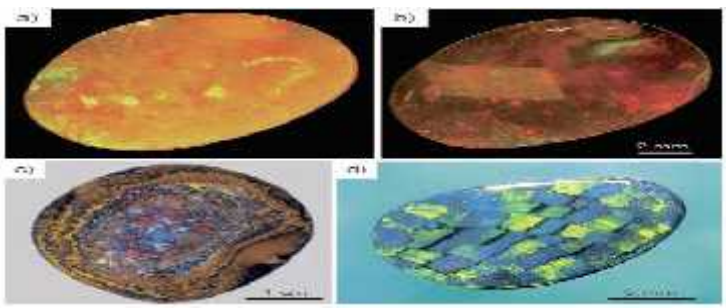


Fig. 7. The color of natural opal.

1.5.4. Refractive index

Refractive index(n) of a material can be expressed as the ratio between the velocity of light in the air (V) and its velocity in the denser material (v), that is, n = V/v. The amount of refraction in the crystal is constant for each specific gemstone. It can be used to identify the type of gemstone. The amount of refraction is called refractive index. It is defined as the proportional relation between the speed of light in air and that of the stone. The decrease in the velocity of light in the stone causes a deviation of light ray. Refractometer is the instrument used to measure the refractive index. The refractive index (RI) of precious opal is in range of 1.43-1.47 and, synthetic opal show above or below this range [25].

1.6. Location of opal in Ethiopia

Australia has been the dominant force in the opal market for over 100 year. During the time as much as 95% of the worldwide opal production has been mined in Australia. Today, Ethiopia is on its way to become the second heavy weight in the opal market. Ethiopia is one of the widely distributed gemstone location in east Africa. Among the gemstones, opal was discovered in 1994 in the Menz Gishe District, North Shewa province around 150 miles (~240 km) northeast of Addis Ababa, the capital of Ethiopia. The opal field lies around 12 miles (~20 Km) north of Mezezo and extends for several square kilometers along the northern side of the Yita Ridge. This opal is mostly in the form of nodules that are originated from volcanic eruption. It has a color of dark brown and had a tendency to easily crack. These qualities made it unpopular in the gem trade [8, 30].

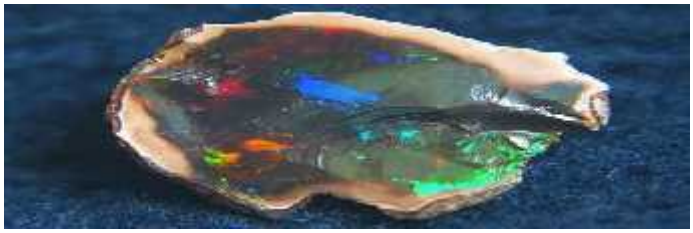


Fig. 8. A nodule of dark body color opal from the Shewa Province Ethiopia [30].

In 2008, a new opal deposit was found near the town of Wegel Tena in the Wello province in the northern part of the country. This opal has vivid play-of-color flashing from a body color of clear, white, yellow, orange, or brown. It is much more stable than the North Shewa opal. The

Wello Province opal which is different from the previous Ethiopian opal is more closely resembled the sedimentary opals of Australia and Brazil, with a light background and often-vivid play-of-color. Wello Province opal, more commonly referred to as "Welo" or "Wello" opal has become the dominant Ethiopian opal in the gem trade [31].

Fig. 9. The Gem-opal recently discovered in Shewa Province, Ethiopia [31].

Fig. 10. The faceted Ethiopian Wello opals [32].

Ethiopian opal is beautiful and its cost is comparable to the opal from the Australia. Nowadays many people look for Ethiopian opal. This huge public awareness has been developed a few years without a major mining company and without promotion of jewelry brand in millions of dollars. This popularity is being driven by the beauty of Ethiopian opal but currently sold at lower prices than Australian opal of similar appearance [31]. Gemological finding indicates that many parts of Ethiopia are potential sources of precious and semi precious stones. These precious and semi precious opal are deposited in different parts of the country. The production of opal becomes a very important endeavor in the gemstone industry in Ethiopia. The activities of artisanal mining are undergoing in Amhara region in Gondar (Gaint), Shewa (Mezezo), Wello (Delenta wereda) provinces and in the Afar region [32].

1.7. Uses and applications of gem opal

For the use of gemstone, most opal is cut and polished to form a cabochon, and these can be used in all form as jeweler. Too thin solid opal combines with other materials form attractive gemstone. Relatively thin layer of precious opal consists opal doublet backed by a layer of dark-colored material, most commonly ironstone, dark or black common opal (potch). This darker color backing emphasizes the play of color, and results in more attractive display contrast that sparks interest, making it another form of opal used in jewellery. The limitation of precious opal for jewellerry application can be somewhat by opal sensitivity to heat. [32].

Devices that are based on the color effects of opals and inverse opals can be found in applications spanning from purely inorganic to bioorganic. Opalescence has been used for displays, photonic inks, switches or sensors, in biometric recognition devices, drug-release or drug resorption monitoring architectures, and glucose sensors.[31]. Metal oxide inverse opals are used in the field of semiconducting gas sensors as sensitive layer. Due to their relatively large specific surface area combined with good pore accessibility, the sensitivity of the sensor can be increased compared to conventional nano-granular layers [33].

1.8. Statement of the problem

From the beginning of human history precious opal gemstone remained the objects of desire. It has been sought for their beauty, their mystic powers and highly esteemed for their value. Opals from Ethiopia attract the gem world by their quality and beautifulness. This creates attention for numerous jewelry auctioneers and dealers. However, the mining operation in our country is dominated by traditional method such as artisanal and low-tech mining system. As a result, the miners are collecting and selling rough gems to the local market and also, the gems are exported as rough to the world market. The challenges are mainly lack of knowledge in sorting and grading, shortage of finance, absence of continuous supply of rough material as well as very few numbers of established lapidary shops. Due to these facts, identification and characterization of natural gem-opal hosted in Ethiopia by traditional and conventional testing method are very difficult for geological world. It needs a careful investigation and takes long period of time. However, accurate gem identification and complete information disclosure are essential in the jewellery trade, to maintain both the commercial value of natural gemstones and the confidence among consumers who are considering gemstone purchases. Therefore,

advanced spectroscopic technique is important to provide enough detail information in order to determine and characterize this natural gem-opal hosted in Ethiopia.

1.9. Objectives of the study

1.9.1. General objective

To identify and characterize the natural gem-opal hosted in Ethiopia (South Gondar) using spectroscopic techniques.

1.9.2. Specific objectives

The specific objectives of the study were-

- ✓ To identify and characterize gem opal hosted in south Gondar using FTIR, XRD and FAAS.
- ✓ To create awareness's on the society about the condition of gem opal in Ethiopia (South Gondar).
- ✓ To identify whether the investigated gem-opal are volcanic or sedimentary origin.

1.10. Significance of the study

Basically studies and research findings are important to contribute some valid knowledge to the well being of the society and for the advancements of the society. The study on identification and characterization of opal gemstone are useful to the opal gemstone importer, retailers, jewellery manufacturers, dealers and to the society. These can be used in awaring the consumer of the fact that many varieties opal gemstones on the market today have been treated or enhanced in order to improve their appearance and to assist regional resources managers in the identification and characterization of the opal gemstone.

1.11. Limitations of the study

The researcher has not deliberately confined his study within one zone. Lack of material and advanced spectroscopic instruments for identification and characterization are the major limiting factors. Had been the study conducted in different zones of the country, the better results would have been observed. The researcher believes that this small study will be a step

stone and contribute its part for those people who are interested in the further study of this topic.

2. LITERATURE REVIEW

Opal (SiO_2-n-H_2O) is one of the hydrated forms of precious gemstone; it has been favored for many centuries. Gemologists are the ones who identify characterize, treat and enhance gemstones. The properties of Chemical composition, Dispersion, Cleavage, Refractive index, Specific gravity, Hardness, Fracture, and Luster etc are used to characterize the gemstone. The stones may exhibit double refraction, luminescence and a particular spectrum that is distinct from other typical stones [8].

There are a limited number of elements and chemical compounds used to determine the physical characteristics of gemstone. The physical characteristics that are generally accepted as being most important are hardness, refractive index and color although thermal stability, chemical stability and toughness are also considered important in many gemstone applications [33]. Gem opal has different physical and chemical properties. Having a broad knowledge about the most important properties of opal gemstone is helpful to the opal gemstone cutter and setters as well as to the wearer of the jewelry and the collector [25]. The diffraction of light caused by the internal structure of opal makes different types of color such as white, gray, red, orange, yellow, green, blue, magenta, rose, pink, slate, olive, brown, and black. Of these hues, the black opals are the rarest, whereas white and greens are the most common. Opals vary in optical density from opaque to semitransparent [24].

The best known in the gem market are the Australia opal. The colors are due to optical diffraction effect from the regularly spaced structure inside. The Mexican has a variety of colorless and clear opal. The best known Mexican opal is fire opal; it has orange or reddish color. The black opal is expensive due its rarity and beautifulness [8].

The existence of trace-element chemistry is important for understanding some physical properties of gem opals, such as color and luminescence, and it is a useful tool for determining their geologic and geographic origin. Aluminum, which substitutes for silicon, is typically the most common impurity in opal [29]. Some “impurities” (i.e., elements present at concentrations above 500 ppm) are Al, Ca, K, Mg, Fe and Na. Elements at concentrations below 500 ppm are named "trace element". These are mainly Ba, Sr, Rb, Mn, and Ti. Green,

blue and pink opal has a higher concentration in several trace elements than other opal (e.g. Mg and Cu for green and blue opals, Mg and Al for pink opal) [28, 29]. Silicon atoms can be substituted by aluminum or iron atoms. The replacement of Si^{4+} by Al^{3+} or Fe^{3+} induces a charge imbalance, which must be compensated by the contribution of divalent or monovalent cations (such as Na^{+}, Ca^{2+} , K^{+}, Ba^{2+}, Mg^{2+}). Therefore, there is a correlation between (Al+Fe) and the sum of the most common divalent and monovalent cations in opal. The substitution is formalized in Equ. 4: [34].

$8(Al^{3+} + Fe^{3+}) + 6\,(Ca^{2+} + Mg^{2+} + Mn^{2+} + Ba^{2+} + K^{+} + Na^{+}) = 27Si^{4+}$..... Equ. 4.

The gemological properties of the investigated opal from Tanzanian showed the UV fluorescence range of 366-254 nm that represents the opal color range from clear green to apple green. The specific gravity values were between 2.11-2.13 and refractive index between 1.439 and 1.458[35].

Studies show that the specific gravity of the Mexifire opal samples was around 1.92-2.06 and their refractive index values were 1.400-1.435 [31]. In addition, the RI value of opal from Bemia, Madagascar is 1.415–1.462 and their specific gravity 2.05–2.38.The gemstone quality of opal comes in a wide variety of colors.

Based on x-ray diffraction (XRD) measurements, opal crystalline order could be categorized into opal-A, Opal-C and Opal-CT. All categories showed different XRD pattern [36]. In the X-ray diffraction pattern of gem opal the main peaks at 2θ = ~28.50 ^{o} and ~31.40 ^{o} are attributed to cristobalite and tridymite phases that showed various degrees of disorder structure. The main peaks are helpful for a rapid identification of gem opal and broad peaks in between 2θ = ~4.9^{o} and 2θ = ~6.8^{o} indicate the presence of clay mineral [29].

A lot of opal sample were collected from different countries and analyzed by using X-ray diffraction. The broad peak at 2θ = ~21.7° in an opal sample of some countries represents opal-A. In the X-ray diffraction pattern of gem opal the five well-resolved peaks at about 2θ = ~20.5°, ~21.6°, ~35.8°, ~44.0° and ~56.5° represents opal-CT. The sharpness and intensity of the main peaks indicate an increasing degree of order [24].

In the XRD pattern, the peak at approximately 2θ = ~21.5° with d-value between 4.0 and 3.8 Å is the characteristic peak position for opal of glass type. This opal do not show sharp diffraction peaks but rather a broad and diffuse reflection. This broad peak is called "glass-

peak" because of its resemblance diffuse peak produced by glass and it merges with background without interruptions.

In the XRD pattern of gem opal sample, the main peak at ~4.09 Å is evidence of opal-CT. The peak at ~2.51 Å, ~2.03 Å, ~1.62 Å and the absence of peaks at around 3.13 Å and ~2.84 Å are characteristic for opal-C [37]. Opal-CT is the predominant silica building block forming the opalline matrix. In addition to opal-CT opal-C is another predominant silica building block forming the opalline mineral. The characteristic relatively intense diffraction peak at around 2.51(9.1) Å represents opal-c [38].

By coupling with other analytical methods, IR spectroscopy is useful for the identification and characterization of gem opal. The mid-infrared IR spectra of opal-CT sample were characterized by spectra features of molecular water and silanol (Si-OH) groups. It consists of a broad absorption band at ~3400 cm^{-1} and 1650-1630 cm^{-1}. Opal-CT show strong absorption band related to Si-O vibration at ~1100, ~790 and ~470 cm^{-1} whereas the overtone weak band and fundamental combination occur at ~2000 and ~1880 cm^{-1}. Opal is in the bands which occur at 1630 cm^{-1} for the opal sample results from the H-O-H bending vibrations of molecular water. The strength of this peak reflects to some extent the content of molecular water in the sample. The impurity of clay mineral also show absorption band at ~3545 and ~692 cm^{-1} [29].

The characteristic IR spectra of water in opal sample are found in between 1500 cm^{-1}- 4000 cm^{-1}. The bands for the H-O-H bending vibration occur at ~1631cm^{-1}. Water and the overtone vibration show bands at ~1800 cm^{-1} and ~1996 cm^{-1}. The bands at ~3410cm^{-1} and ~3650 cm^{-1} are related to the O-H stretching modes of hydrogen bands and of isolated silanol groups, respectively. The bands in the region of 500-1500 cm^{-1} are mainly related to asymmetric stretching and bending modes of the SiO_4 tetrahedral. The bands at ~2400 cm^{-1} indicate the asymmetric stretching modes of CO_2 in air [39].

The chemical structure of synthetic opal prepared with different concentration of tetraethyl orthosilicate (TEOS's) show different FTIR spectra. The FTIR spectra of those opals including before and after thermal treatment show their own absorption spectra. The three major bands occur at around 470, 790 and 1100 cm^{-1} can be assigned to O-Si-O and Si-O-Si bending, symmetric stretching and Si-O asymmetric stretching vibration, respectively. The presences of intense absorption peak centered at ~1100 cm-1 indicate Si-O-Si stretching bands. This confirms the formation of a network structure inside the opal [15]. In case of the opal

synthesized by adding the high concentration of TEOS and the heat treated opal show very sharp peak at ~1,100 cm^{-1}. These indicate that the degree of crystallinity in this opal is higher than the opal synthesized by other conditions.

The FTIR spectra peak around 1,600 cm^{-1} is due to H-O-H bending vibration of molecular water related to two water species, H_2O and Si-OH group. The absorption band around 3400 cm^{-1} is due to the Si-OH group. The FTIR spectra of all synthetic opal after heat treatment present the spectra feature similar with those of natural common opal. However, small absorption band occur at ~950 cm^{-1} attributed for Si-OH stretching (silicate form) present only in synthetic opals. Therefore, it can imply that this band can use for distinguishing between natural and synthetic common opal [21].

The infrared spectra recorded for the synthetic and natural opal samples displayed similar features in the range 6000-400 cm^{-1}. The samples had absorption band in the region of ~5350-5000 cm^{-1}; this feature also consists of sharp peaks on the transmission. A hump was observed in the ~4600–4300 cm^{-1} range, often with small peaks, in all of the synthetic opal samples but the absence of the absorption feature at ~4600–4300 cm^{-1} may provide a useful identification criterion for determining natural origin. The detector was saturated by strong absorption at wave numbers below approximately 4000 cm^{-1} [32].

In one of the first infrared studies of opal-CT, noted that prominent absorption bands for cristobalite at 620 and 385 cm^{-1} were absent from the spectrum, which was very similar to that of tridymite and silica glass. But opal-CT show none of the diagnostic absorption bands α-cristobalite at 620, 520, 385, 300 and 145 cm^{-1}, where as the bands attributed to tridymite (amorphous silica) at 11o4, 790 and 474 cm^{-1}[40].

Opal is characterized by a multi component broad absorption band centered at about ~3470 cm^{-1}, due to the OH stretching vibration of water molecules, as well as the water bending vibration at ~1640 $cm^{-1.}$ The other three bands at ~1100, ~790 and ~480 cm^{-1} are common to all silicates with tetrahedrally coordinated silicon and are related to the fundamental Si-O stretching vibration. In particular, the ~1100 and ~790 cm^{-1} bands are generally assigned, respectively, to antisymmetric and symmetric Si-O-Si stretching, whereas the 480 cm^{-1} band is related to O-Si-O bending vibration [35]. The peak at ~1080cm^{-1} can be assigned to the Si–O bond structure and also the additional peak between ~1000 and ~1080cm^{-1} is thought to be due to ≡Si–O–Si≡

stretching vibrations. The peak around ~3450 cm^{-1} for O-H stretching in fire opal or H-O-H stretch in fire opal , ~1910 cm^{-1} for Al-O vibration, ~1640 for O-H bending vibration. The peak around ~1180 cm^{-1} and ~790 cm^{-1} for asymmetric stretching Si-O-Si and stretching vibration for symmetric Si-O-Si respectively [38].

Study on the gemological property of Hungarian opal showed the specific gravity value 2.01-2.10 and the refractive index value 1.439-1.442. The trace element content of Hungarian opal was reported to be around 200-300 ppm. These values are low in comparison with those of opals reported worldwide. The most abundant elements are Ca (90-178 ppm), Al (67-125 ppm), Na (22-95 ppm), K (15-44 ppm), with lower amounts of Fe (4-14 ppm), Mg (3-10 ppm), Sc (2-3 ppm), Cr (1,4-2.5 ppm). Cromophore elements like Fe, V, Cr, Cu, Co, Ni are low or absent and, therefore, the investigated samples appear white [41].

The investigated opal samples from Tanzania show the most abundant trace element Ni (between 3800 and 20300ppm). All the other elements are present in much lower amounts; their total sum is approximately 1000 ppm. These values are low compared to that of many other opals in the world. Other elements in insignificant quantities are Mg (~500 ppm), Ca and Zn (~100 ppm), Cr (~80 ppm), Co (~40 ppm), Fe (between 6 and 30 ppm) and Na (~10 ppm). It is noteworthy that elements such as Al, Na, and K which are often present in high amounts in the opals worldwide appear instead very low in the Tanzanian opals. Al is frequently the most abundant impurity in opal and substitutes locally for silicon; but the imbalance charge is compensated by the ingress of monovalent or divalent cations such as Na^{+}, Ba^{+}, Mg^{+} and Ca^{+} [24].

3. MATERIALS, METHODS AND ANALYSIS

3.1. Instruments, Apparatus, Reagents and Standards

3.1.1. Instrumentation and Apparatus

A refractometer of United Kingdom manufacture was used to measure the refractive index (RI) with an optical contact liquid value between 1.79 ±0.05 at room temperature. The specific gravity was measured by heavy liquid test (Lithium salt with specific gravity value 2.57 (UK)). The instruments of MOHS HARDNESS PENCILS (UK) were used to measure hardness value of gem-opal sample. Agate mortar and pestle were used to powder the opal sample. A sieve with 0.1mm size was used to sieve the powdered opal sample. An electronic digital balance (Denver instrument company, USA) was used to weigh the powdered opal sample. Borosilicate Erlenmeyer flask and hot plate were used to digest the opal sample. The pipettes (1mL, 2mL, 5mL), 100mL, 50mL volumetric flask, 50mL of Erlenmeyer flask and beakers were used to dilute the standards and samples solution. An atomic absorption spectroscopy (BUCK SCIENTIFIC MODEL 210 VGP, U.S.A.) equipped with air/acetylene flame, with a hallow cathode lamp for the determination of Manganese, iron, calcium, zinc, copper and magnesium were used.

A 65 FT-IR spectrometer PerkinElmer (U.S.A) operated at transmittance mode and equipped with a 4x beam condenser and scanning speed auto (4mm/sec) at a resolution of $4cm^{-1}$ in the wave length range of 4000-400 cm^{-1} was used for recording the infrared transmission spectra using the KBr pellet method.

Minflux 600 powder diffractometer Rigaco (USA) equipped with CuKα radiation (λ = 1.5418 Å) and a scan speed of 1°/min and in the range between 10-70° 2θ was used to collect X-ray powder diffraction data for qualitative and semi qualitative analyses of the mineral phase in the opals sample and host rocks.

3.1.2. Chemicals and Standard Solutions

Chemicals that were used in the analysis are analytical grades. KBr (obtained in the PerkinElmer (U.S.A) accessories and consumable kit), 48% of HF (Anala R, PARK: Hydrofluoric acid Solution Northampton scientific Laboratory supplies, U.K), 69-72% (Analytical R, IMO: Nitric acid solution BDH Laboratory supplies, England) of HNO_3,

35.38% of HCl (Blulux®, laboratory reagent, India) and 30% of w/v H_2O_2 (MS Laboratory Reagent, Medical PVT.LTD, New Delhi) were used to digest the opal samples. Stock standard solution of the metals Ca (1000 mg/L), Fe (1000 mg/L), Mn (1000 mg/L), Mg (1000mg/L), Zn (1000mg/L) and Cu (1000mg/L)) prepared for an atomic absorption spectrophotometer (BUCK SCIENTIFIC MODEL 210 VGP, U.S.A.) were used for the preparation of calibration curves for the determination of metals in the sample. Distilled water was used for cleaning of glassware and dilution of sample solutions.

3.2. Location and accessibility

The sample was collected from Amhara National Regional, South Gondar Administrative Zone Technical Vocational Enterprise Development Department, Debretabor.The office collect the sample in Tach Gaint localities. This research site is situated in Amhara Administrative Region, South Gondar Zone, specifically in Gaint Woreda; locally known as Tach Gaint, which are 767 km far from Addis Ababa which is the capital city of Ethiopia. These study area can be reached as; Addis Ababa_____ Bahir Dar _____ Debra tabor _____Gaint Woreda_____Tach Gaint respectively.

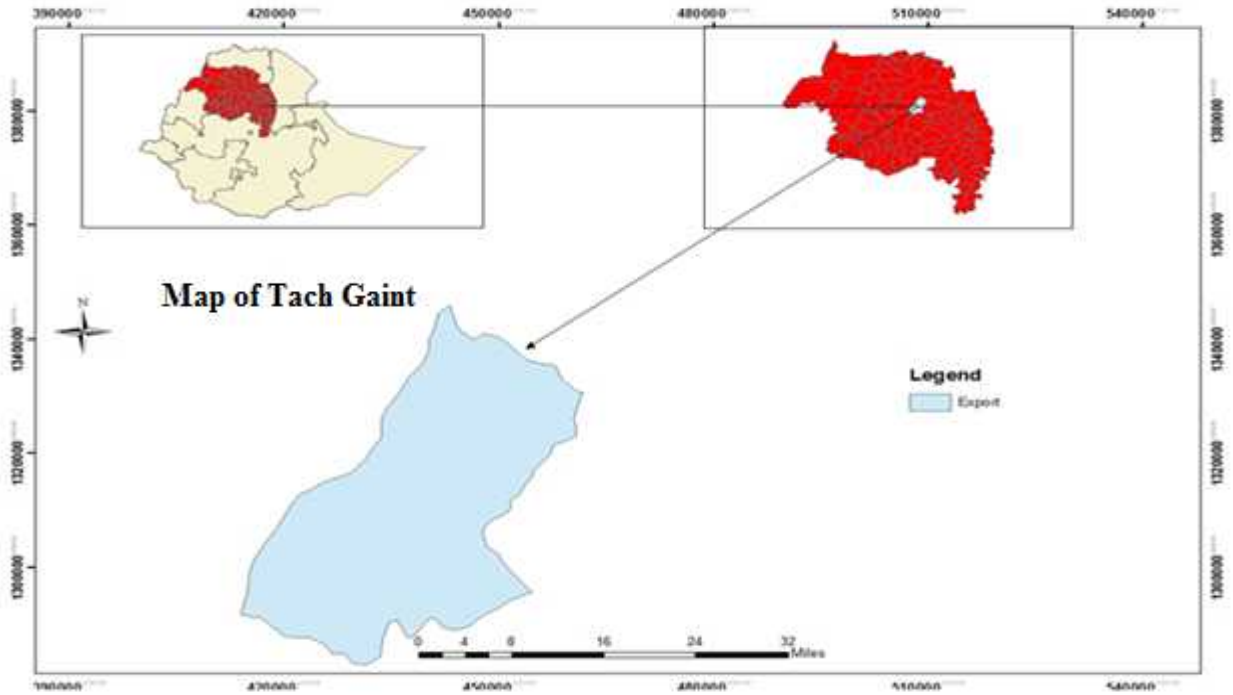


Fig. 11. Map of study area (From GIS)**.**

3.3. Experimental design

During the experiment, three replicate samples of natural gem-opal were conducted for AAS spectroscopic technique and one sample for FT-IR and XRD spectroscopic techniques. But the samples have equal size and the same color. In this experimental design the physical properties of the sample, such as specific gravity, hardness, and refractive index were determined by heavy liquid method, MOH'S HARDNESS PENCILS, and refractometer respectively.

3.4. Procedure

3.4.1. Collection of opal sample

The sample of natural gem-opal was collected from the South Gondar Administrative Zone Technical Vocational Enterprise Development Department, Debretabor. The samples were all gems, common or precious opals, opal-A or opal-CT and come from volcanic or sedimentary environments. Their body color spans almost the entire visible spectrum: yellow, orange, red, white, brown and blue.

3.4.2. Determination of gemological properties

The physical properties of the samples were measured in order to verify that the samples are real opals or not. These gemological (non-destructive) characterization tests were performed on representative sample. The tests were performed at Gondar poly-technique gemological testing laboratory in Maraki branch. For these purpose a refractometer of UK manufacture was used to measure refractive index (RI) with an optical contact liquid of 1.78±0.05 RI at room temperature and the specific gravity was measured by heavy liquid method using (Lithium salt). "The instruments of MOHS HARDNESS PENCILS" were used to determine the hardness of the opals.

3.4.3. Sample preparation

Following the procedure in [42], the collected sample was washed with distilled water; air dried and grounded in to fine powder using agate mortar and pestle and finally the powder was sieved with a 0.1 mm sieve. For FAAS analysis, the powder opal sample (0.5g) was weighed and put in to three replicate 50mL borosilicate glass of Erlenmeyer flask and 5mL conc. 69-

72% HNO_3, 2mL 35.5% HCl, 1mL 30%w/v H_2O_2 and 2mL of 48%HF were added in each flask. Then after each Erlenmeyer flasks were heated on hot plate and the solution evaporated near dryness. After that 2 mL 48% HF was added on each flask and heated for a few times until precipitation of SiO_2 is eliminated as SiF_4 vapors. Cooling down to the room temperature, 2mL conc. HCl and 5 mL of distilled water were added then the solution were transferred in to three (100mL) of volumetric flasks and filled up with distilled water up to mark. The FTIR analysis was carried out by taking powdered gem-opal sample exactly 2mg (using electronic digital balance) and mixed with 200mg KBr in order to prepare circular pellet.

The XRD patterns analysis was carried out by taking powdered natural gem-opal sample and transferred it into sample holder of the instrument.

Fig. 12. The natural gem opal samples from south Gondar with their host Rocks**.**

3.5. Spectroscopic Technique and Optimal Condition

3.5.1. For trace metal determination using FAAS

To analyze the sample on the FAAS, the instrument was adjusted in appropriate manner such as, wave length selector; hallow cathode lamp, slit width, fuel valve and vertical and horizontal position of burner head. The absorbance of the analytic line is a function of several parameters, burner head position (vertical, horizontal) and flow rate of used gases. Optimal values of these parameters are those, which yield maximum absorbance value. The optimization procedure

was carried out by studying the effect of one parameter while keeping the others constants at appropriate values.

To carry out this study the acetylene and airflow rate were kept constant. Before the samples were run in BUCK SCIENTIFIC MODEL 210 VGP, FAA spectrometer, the presence of precipitate in the sample as well as standard solution were checked and total inspection was done by measuring the absorbance of distilled water. For the determination of trace metals on the sample of gem-opal, six standard metal solutions (table-1) were prepared by diluting the stock solution with distilled water. A blank solution and the six standard solutions as well as three replicate sample solutions were run in flame atomic absorption spectrophotometer (BUCK SCIENTIFIC MODEL 210 VGP, U.S.A) within adjusted hallow cathode lamp of instruments for each element and direct reading of the metal absorbance were recorded. Finally the six point's calibration curves were established. The operating conditions of FAAS employed for each analyte are given in table-2.

Table 1. Instrumental operating conditions used for flame atomic absorption spectrometer.

Elements	Wave length in (nm)	Current (mA)	Slit width in (nm)	Detection limit (mg/L) from the instrument's operator mnual	Energy (J)
Mn	279.5	3	0.7	0.03	4.253
Zn	213.9	2	0.7	0.005	3.302
Fe	248.3	7	0.2	0.05	3.844
Mg	285.2	1	0.7	0.005	4.501
Ca	422.7	2	0.7	0.05	0.990
Cu	324.7	1.5	0.7	0.01	3.869

3.5.2. For characterization using FT-IR

Before the sample was run in 65 FT-IR spectrometer PerkinElmer (U.S.A), the instrument’s total inspection was done by measuring absorbance of the standard polystyrene film and empty sample compartment turn by turn. A back ground (KBr) measurement was done. By following the above sample preparation method, powdered FT-IR spectra was collected at Addis Ababa University on 65 FT-IR PerkinElmer (U.S.A) spectrometer equipped with KBr beam splitter;

2mg of the sample was weighed using electronic balance and mixed with 200mg of KBr. The mixture was further powdered so as to mix well, and then the pellet was prepared and finally placed in to a sample holder of the instrument. Then the spectra were collected by 65 FT-IR spectrometer PerkinElmer (U.S.A), operated at transmittance mode in the range 4000-400 cm^{-1} and the average scan speed 4 mm/sec for both sample and background with a 4 cm^{-1} nominal resolution.

3.5.3. For characterization using XRD patterns

To analyses, opal sample by using XRD pattern, the sample was converted in to powdered form and the sample was inserted in to the sample holder of the instrument, the spectra was collected at Addis Ababa University on minflux 600 powder X-ray diffractometre Rigaco (USA). The instrument was adjusted with Cu tube and a graphic monochromator with CuKα radiation (λ=1.5418Å) and a scan speed of 1°/min in the range between $2\theta = 10\text{-}70°$.

4. RESULTS AND DISCUSSION

4.1. Gemological properties

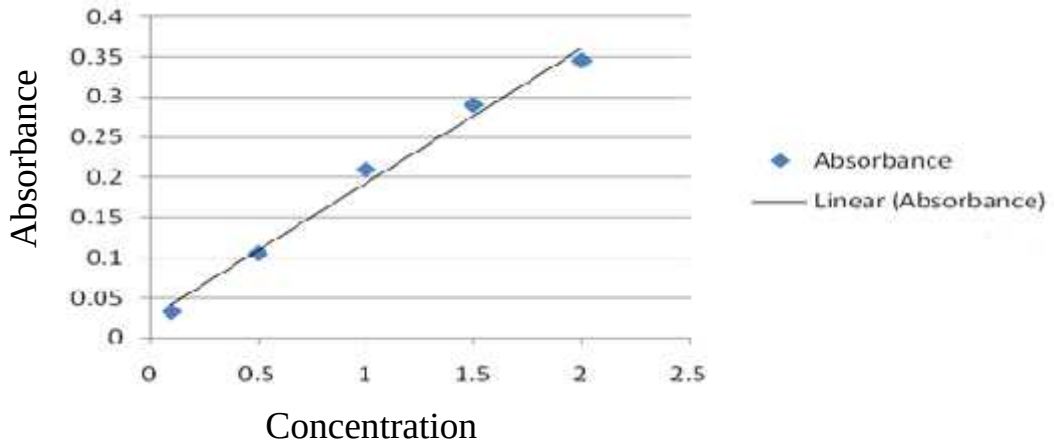
To verify that the investigated rough gem-opal sample was indeed opal, non-destructive gemological characterization tests were performed on representative sample. First average specific gravity value of representative sample was measured by heavy liquid method using (Lithium salt). The value is between 2.02-2.3 i.e., in the range of literature data [22, 37]. Second, because of optical character and optical sign, refractive index values of representative sample was determined by using standard refractometre device with an optical contact liquid of 1.79 RI. Therefore the refractive index values of investigated sample vary between 1.437-1.445 and similarly with specific gravity, their values are comparable with literature data [31, 35, and 41]. Third, "the instruments of MOHS HARDNESS PENCILS" were used to determine the hardness of the opals; the value is between 5.5 and 6 which are comparable with reported data of [25]. In the visible spectrum their body color has yellow, orange, red, white, brown and blue. Results of all these gemological testing values indicate that the sample is indeed opal.

4.2. Flame Atomic Absorption Spectroscopic analysis

After the optimized conditions were done, the analytical calibration curves were plotted by using prepared standard solutions for every element (Mg, Zn, Cu, Fe, Ca, and Mn). The standards were prepared by diluting of the stock solution containing 1000 µg/mL by distilled water for each element.

Table 2. Series of working standards for determination of trace metals in opal sample.

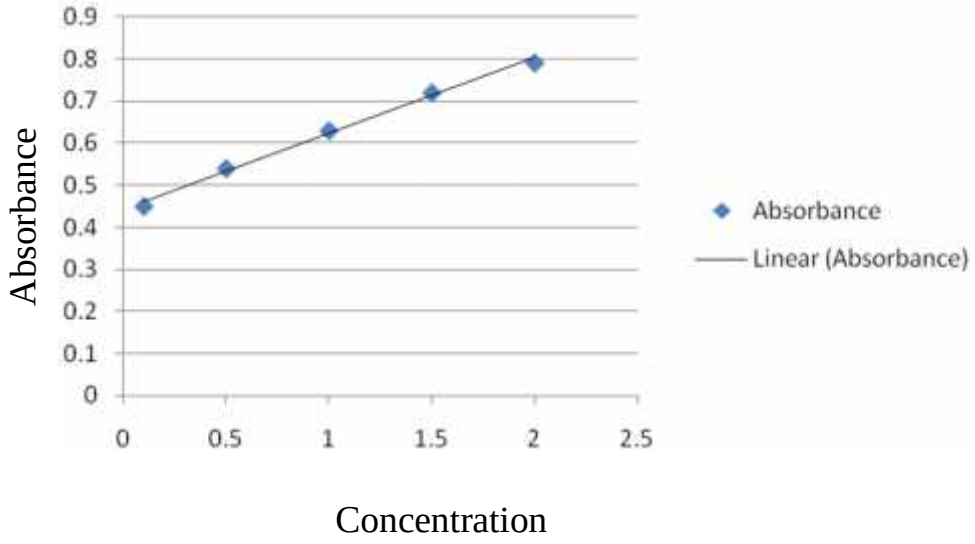
No	Element	Concentration of standards in µg/mL	Correlation coefficient (R)
1	Mn	0.1, 0.5, 1, 1.5, 2	0.919
2	Zn	0.1, 0.5, 1, 1.5, 2	0.946
3	Fe	1, 3, 5, 7, 9	0.960
4	Mg	0.5, 1, 1.5, 2, 2.5	0.958
5	Ca	0.5, 1, 1.5, 2, 2.5	0.808
6	Cu	0.1, 0.5, 1, 1.5, 2	0.991



Y = 0.168x + 0.025

R^2 = 0.987

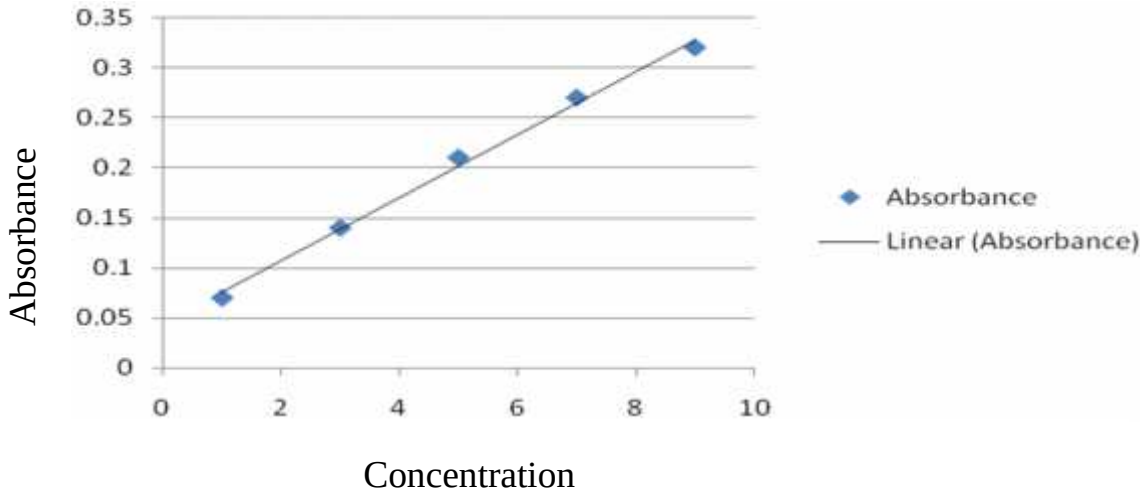
Fig. 13. Calibration graph for manganese standard solution.



Y = 0.179x + 0.443

R^2 = 0.994

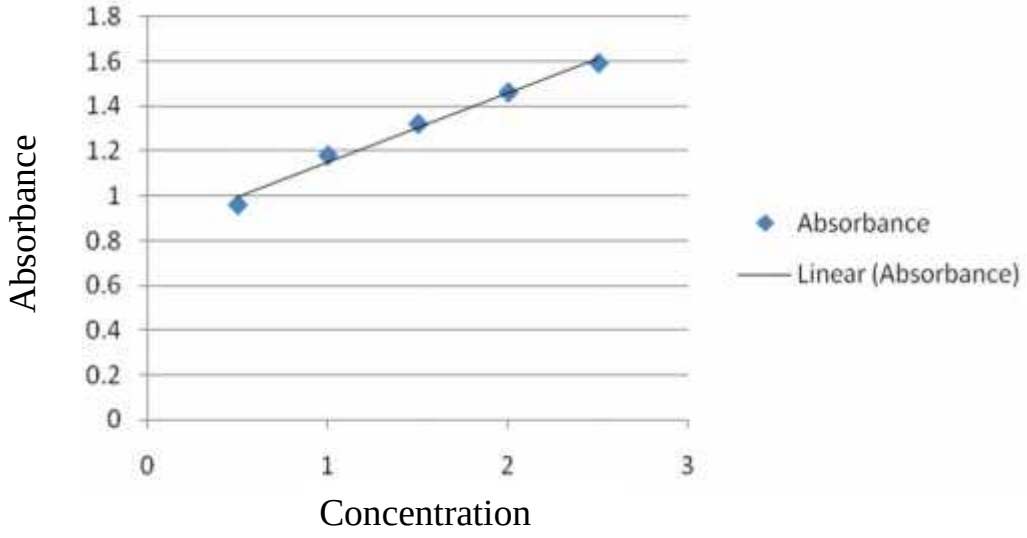
Fig. 14. Calibration graph for zinc standard solution.



y = 0.031x + 0.044

R^2 =0.995

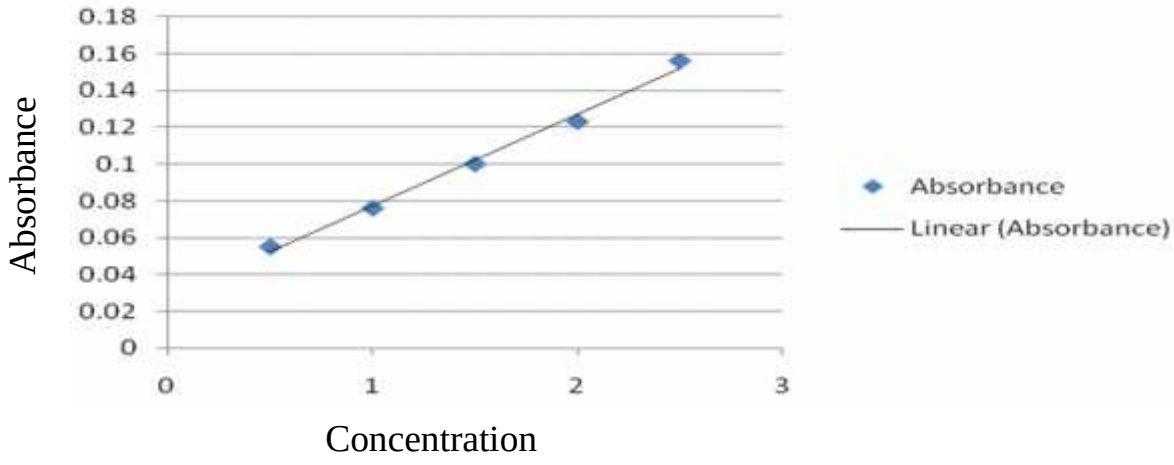
Fig. 15. Calibration graph for Iron standard solution.



Y =0.308x +0.84

R^2 =0.987

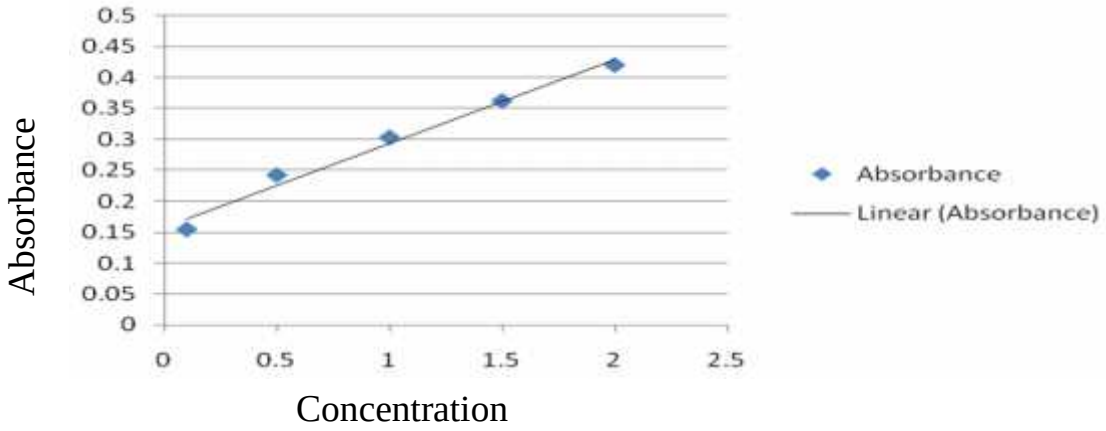
Fig. 16. Calibration graph for magnesium standard solution.



Y = 0.049x + 0.027

R^2 = 0.992

Fig. 17. Calibration graph for calcium standard solution.



Y=0.135x + 0.158

R^2 = 0.982

Fig. 18. Calibration graph for copper standard solution.

Table 3. Concentration of determined trace element in opal sample.

Trace elements	Mn	Zn	Fe	Mg	Ca	Cu
Concentration in mg/L(ppm)	0.214	1.1	3.021	0.866	1.557	0.163

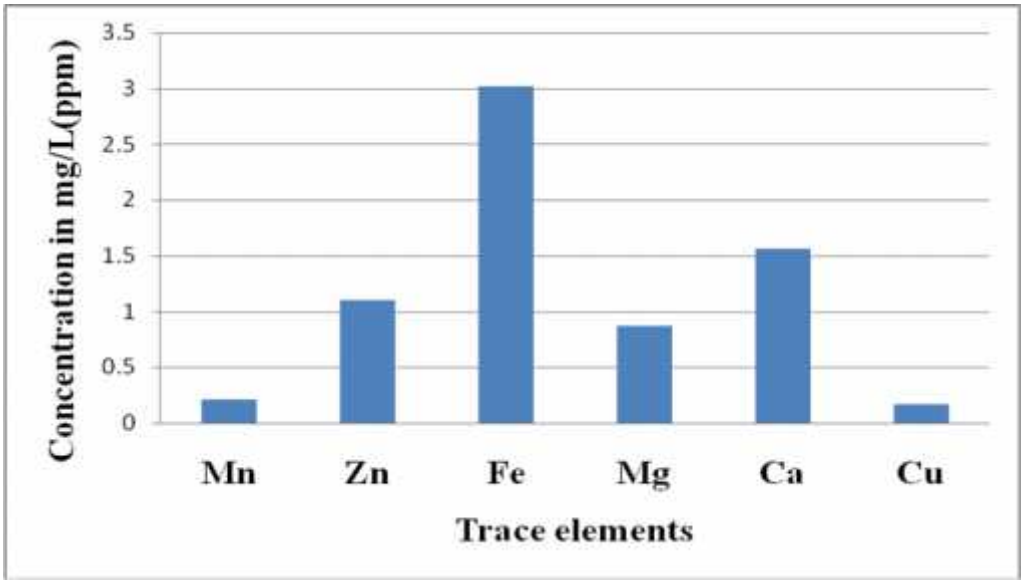


Fig. 19. Histogram comparing concentrations of metals in ppm

The body color of opals (when it could be established) has so far always been linked to inclusion. It can be assume that the color is effective due to the inclusion, their nature remains uncertain, but can be constrained to a few possibilities [34]. Also, the existence of trace-element chemistry is a useful tool for determining their geologic and geographic origin [28, 29]. The results of determined concentrations of trace elements in the investigated gem-opal sample from south Gondar are given in table-3 above.

In this study it has been found out that the opal sample of south Gondar has the high content of Fe (Table-3). According to studies conducted previously, the orange color is due to the high contents of Fe trace element and the light brown color is associated with small contents of Mn in the opal sample [34]. The blue color is associated with the presence of Cu, Mg and Zn silicate inclusion. In this study, it is also observed that the high intensity of the orange color (from yellow to orange to red to "chocolate"-brown) correlates with the Fe concentration. No other element correlates with Fe. The white color is due to presence of calcium metal and the red (yellowish) color observed in the opal sample is associated with +3 oxidation state of iron [35]. Calcium is the only element that varies significantly with the geographic origin of opal. Opals from Ethiopia are easily distinguishable from other opals because of their high value in Ca concentration [23, 34].

4.3. Fourier Transform Infrared Spectroscopic analysis

The FT-IR spectrum of gem-opal sample (Fig.20) was characterized by spectra features of molecular water and silanol (Si-OH) groups. The spectra collected in the range 4000-400 cm^{-1} are absolutely compatible with those already in the literature data of similar sample [29].

The infrared spectra of the investigated sample of gem-opal shown in (Fig. 20) are characterized by a multi component broad absorption bands centered around 3460 cm^{-1}, the OH stretching vibration of water molecules as well as the water bending vibration occur in the range of 1640 cm^{-1}-1625 cm^{-1} are compatible with literature data of [23, 24]. In the low frequency region from 2000 cm^{-1} up to 500 cm^{-1}, the investigated sample has three intense absorption bands centered around 520 cm^{-1}, 800 cm^{-1} and 1020 cm^{-1} and it is comparable to literature data. These bands are due to the absorption of silicate frame work vibration [24, 35] and common to all silicates with tetrahedrally coordinated silicon, it related to Si-O stretching [35].

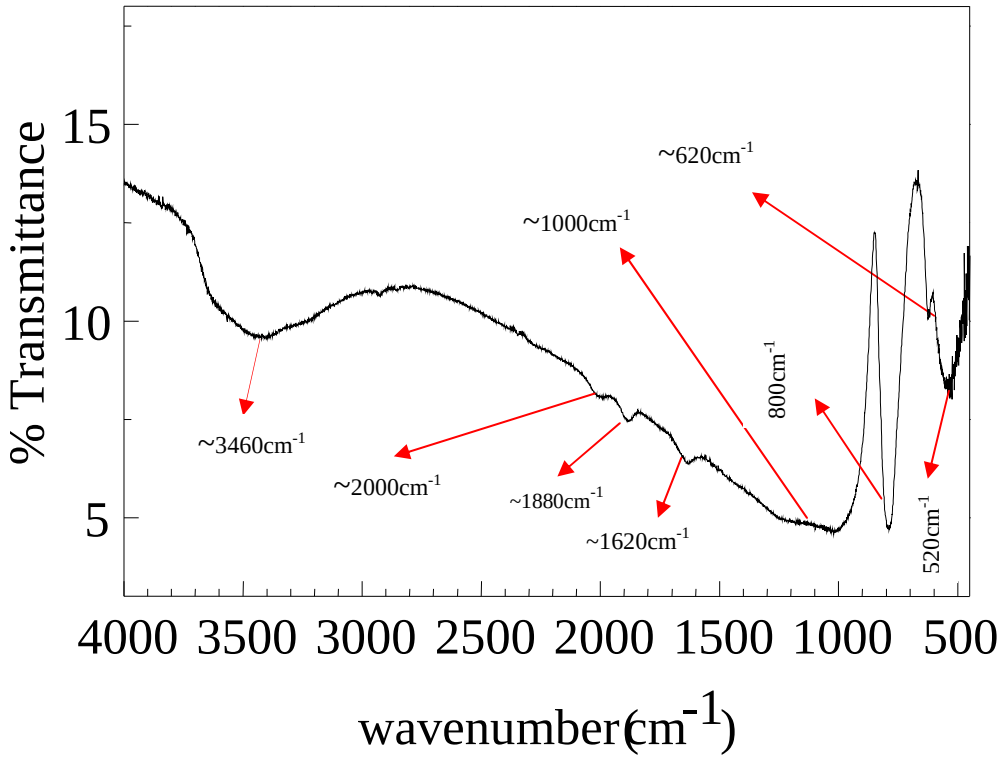


Fig. 20. The FT-IR spectra of the analyzed opal sample

In particular, the bands occur around 1020 cm^{-1} and 800 cm^{-1} are generally assigned to antisymmetric and symmetric Si-O-Si stretching vibration respectively, whereas the band centered near 520 cm^{-1} is related to O-Si-O bending vibration. These are much related to the literature data of [23, 35], in which the band centered around 470, 790 and 1100 cm^{-1}. The presence of intense absorption peak centered around 1020 and 800 cm^{-1} (Si-O-Si) confirms the formation of a network structure inside the opal as already pointed out in the previous research [15]. FT-IR spectra region for CO_2-free opal show only two broad band's at around 2008 cm^{-1} and 1880 cm^{-1}[24]. Similarly the FT-IR spectra of investigated sample has two weak bands around 2000 cm^{-1} and 1880cm^{-1} ,therefore these two weak bands indicate the absence of CO_2 in opal sample and as it is discussed in literature data [29], these band formed due to overtones and combinations of Si-O fundamental vibration. The spectra of opal analyzed in these studies are very similar to that of opal-CT and opal-C stacking sequence (fig. 20). Because, the peak at ~620 cm^{-1}, typical of opal-C, is present and the wider band centered at ~1020 cm^{-1} is a typical characteristics of opal-CT. In conclusions, FT-IR data show that the investigated sample is

both opal-CT and opal-C opaline mineral, comparable in literature data of [35]. The spectra of volcanic opal, in general, tend to be sharper than those of sedimentary origin. This is consistent with the idea that the opal from sedimentary origin is amorphous in character while the opal from volcanic origin contains a high degree of crystallinity [11]; these indicate that the sample is volcanic origin.

4.4. Powdered X-Ray diffraction patterns analysis

Gemological properties and mineralogical composition of south Gondar gem-opal can be identified by different spectroscopic techniques. The mineralogical assemblage of host rocks could be determined by XRD pattern; investigation is mostly made by feldspars [23] and these XRD patterns are used to identify silica phase building components, such as opal-CT, opal-C and opal-A.

In this study the numerical data obtained from XRD analyses of South Gondar opal sample was related to those studied in other countries' opal sample [24].

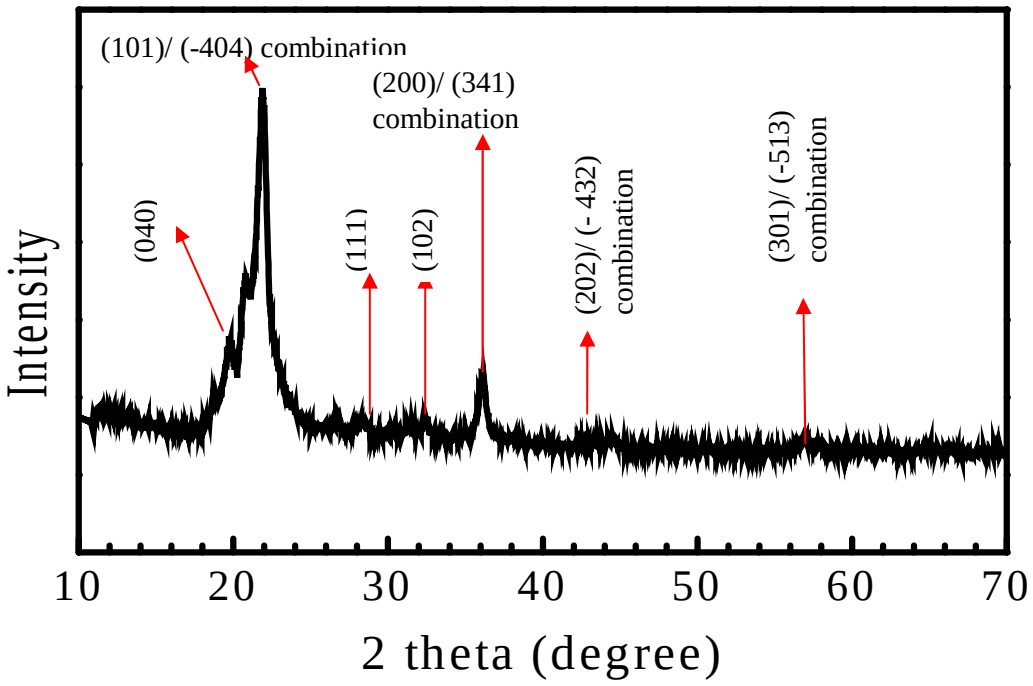


Fig. 21 The XRD patterns of the investigated gem-opal

The comparative matching technique for XRD pattern is based on the positions of peaks at 2θ values in the range between 10°-70°. The XRD patterns of opal-CT show five resolved peak at

2θ = 20.5°, 21.6°, 35.8°, 44° and 56.5° which could be attributed to the (040), (101)/ (-404), (200)/ (341), (202)/(-432) and (301)/(-513) planes respectively and opal-C show two weak bands at 2θ = ~ 28.5° and 31.4° which could be attributed to (111) and (102) planes respectively in the range between 2°- 65° in [24, 43].

In this study, the investigated opal sample in the range between 10° to 70° shows similar five resolved peaks 2θ = 20.65°, 21.8°, 36.05°, 44.5° and 56.85° which could be attributed to the (040), (101)/ (-404), (200)/ (341), (202)/(-432) and (301)/(-513) planes respectively and similarly two weak bands at 2θ = ~28.5° and ~31.4° which could be attributed to (111) and (102) planes respectively. Therefore, the observed XRD patterns of the investigated gem-opal sample were matched with distinctive silica phase building components of both opal-CT and opal-C. X-ray diffraction (XRD) powder pattern yielded by opal-CT is characterized by three broad reflections, the most intense of which occurs around about (21.6°-22.00°) in 2θ with subsidiary peak or shoulder around about (20.7°) and there is also weaker reflection band occur around about (35.9°), as already pointed out in the previous research [40, 44]. In addition, the characteristic band centered around 21.7° and three shoulder peaks represents opal-CT [42]. As described in literature data of [29] the cristobalite opal structure has two important peaks occurs at ~28.5° and 31.4°, which allow for a rapid identification. The XRD patterns of opal-A show only one very broad peak around 21.7° [24], while, under this studies the sample cannot show this distinctive silica building components of opal-A. Therefore, based on the above evidence the studied opal sample can be categorized under opal-CT and opal-C as a result it consist of structural disordered opal-CT and ordered opal-C stacking sequences in opal. It is one of the most important predominant silica building block that forming opaline matrix component [38]. The crystallinity differentiation between volcanic and sedimentary opal may be directly related to the grain size of these silica phase building components [42]. Usually opal-CT and opal-C are found in volcanic environment, while opal-A are typical of both sedimentary and hydrothermal environments [23], therefore the investigated gem-opal sample are found in volcanic environments. The main peak sharpen occurred at around 21° indicating the degree of ordered in opal structure and the broad band at 2θ = 10°-18° indicates the presence of clay mineral. These data is compatible with literature data [24, 29]. From the XRD measurement, we have confirmed that the investigated gem-opal is categorized under opal-CT and opal-C. And also we have confirmed that the investigated gem-opal is volcanic origin.

Table 4. The result of investigated opal sample obtained from X-ray diffraction pattern.

Structural group	2Θ values	*(hkl)* values on plane	Classification
Opal-CT	~20.65°	(040) of α-cristobalite	Volcanic
	~21.8°	(101) of α-cristobalite and (-404) of α-tridymite	
	~36.05°	(200) of α-cristobalite and (341) of α-tridymite;	
	~ 44.5°	(202) of α-cristobalite and (-432) of α-tridymite	
	~ 56.85°	(301) of α-cristobalite and (-513) of α-tridymite.	
Opal-C	~28.5°	(111) of α-cristobalite	Volcanic
	~31.4°	(102) of α-cristobalite.	

Further work

In view of present results, some further directions of research appear manifest. As in all preliminary studies, results confirmed by further analyses, in particularly the contents of host rock and trace elements. However, the consistency of the present results suggests the conclusion may have some merit. In addition, this spectroscopic approach does not fully classify about restrictive chemistry of the opaline matrix components formation mechanism. We know only that they carry silica and some other impurities and trace elements. This is actually a broad question, relevant not only to opal but also to other silica minerals. Further studies will need to explore this and possibly further parameters in order to provide complete study of the opal samples.

5. CONCLUSION

South Gondar opal is a recent discovery in Ethiopia, which is located around Tach Gaint it has a great importance in economy and now sold as raw materials or as cabochon cut in the gemstone markets. The white and yellow colors sample were analyzed in this work and can be considered as precious as they show the phenomenon of play of color.

Determinations of gemological properties are important in order to verify indeed opal or not. Therefore the performed physical analysis shows that the hardness value is in between the range of 5.5- 6, the refractive index value in the range of 1.437-1.445 and the specific gravity value is in the range of 2.02-2.3; the values are comparable with literature data.

The composition of trace elements influences some physical properties of gem-opal. Not surprisingly, color is often dependent on chemical impurities; almost all color of opal is colored by impurities, while some are colored by mineral inclusion. In this study, it is observed that the intensity of orange color (from yellow to orange to red to "chocolate"- brown) correlates with the large amount of Fe concentration and white color correlate with large amount of Ca concentration.

It is also presented that FT-IR spectroscopy could not discriminate between the difference color varieties of the studied opal samples. However, the presented spectra data for opal sample have a significant contribution in their identification and characterization. This spectroscopic technique is important to identify their functional group in the opal formation.

XRD patterns are used to determine mineralogical assemblage of host rocks, under investigation of feldspars. It also used to classify the base silica building components in to opal-A, opal-C, and opal-CT. Microcrystalline silica structure consists of nano sized base silica building components of mainly opal-CT and opal-C. These nano-grain sizes of silica building components can be measured using graphical modeling technique method from X-ray diffraction numerical data and peak position. Under these studies, the XRD data of gem-opal sample are related to both opal-C and opal-CT of base silica building components and these are mainly found in volcanic environments.

6. RECOMMENDATION

Gemstones mining technology in our country is a new practice. It is very surprising and irritating when we compared our country Ethiopia with the other countries in this technology. The mining systems are dominated by artisanal mining operation. These artisanal mining have neither indigenous knowledge of mining nor technical skills. This would create economically unfeasible mining system. And also, a miner is lack of information on site identification and availability of minerals deposits which made mining just a random operation in most cases. The consequences could be simply wastage of labor, energy and resources, in addition to environmental damage. This artisanal mining technology have also the market related challenges such as price fluctuation and illegal trade, lack of standardization and cheating in the measuring scale of the minerals. Therefore, the governments have to give full attention to the mining sector, by providing professional budget and logistics at all regional, zonal and woreda levels, improving marketing system, technical and skill training and also create modern mining operation technology. To make it clear, we have gemstones but still we are not in a position in exploiting these useful minerals. So what is expected from us especially from scholars? It is the opinion of the researcher that geologists, chemists, gemologists and other concerned bodies are expected to further work on in exploring, characterizing, identifying, treating and promoting the gemstone technology to fill the knowledge gap and to boost the country’s economy.

7. REFERENCES

[1]. Amena, Leta. "Geology and Genesis of Gold Mineralization in Kushmagane Area, Assosa Woreda, Western Ethiopia." PhD diss., Addis Ababa University, 2016.

[2]. Senior, B. R." Weathered-profile-hosted precious opal deposits."*AGSO Journal of Australian Geology and Geophysics* 17 (1998): 225-228.

[3]. Amhara National Regional State Education and training development Agency (Bahirdar, Ethiopia). Stone makes human being to exist as a human being (Amharic version) (Pamphlet).

[4]. Geological survey Ethiopia; https://ethiopiaobservatory.com/2013/04/23/ who-Is benefitting from-Ethiopia-global-brand name-opals/ Accessed on Wednesday, April 01, 2017, 9:12:47 PM.

[5]. U.S. Department of the Interior (2016) U.S. Geological Survey ETHIOPIA: 2013 Minerals Yearbook http:// minerals. Use. gov/ minerals /pubs/ country/ 2013/ myb3-2013-et.pdf.

[6]. GIA-Gemological Institute of. America, http://www. com/jewelry/gemology evaluation khulsey equipment.html (Accessed on Wednesday, October 07, 2009, 9:12:47 AM).

[7]. Smallwood, A. G., P. Thomas, and A. S. Ray. "Comparative analysis of sedimentary and volcanic precious opals from Australia." *Journal of Australasian Ceramic Society* (2008).

[8]. Olga Kavtreva "Structural characterization of photonic crystals based on synthetic and natural opals" Seminar: July 19, 2005.

[9]. Ilieva, Albena, Boriana Mihailova, Zdravko Tsintsov, and Ognyan Petrov. "Structural state of microcrystalline opals: A Raman spectroscopic study."*American Mineralogist* 92, no. 8-9 (2007): 1325-1333.

[10]. Knauth, L. P. "Silica: Physical Behavior, Geochemistry and Materials Applications." (1994): 233-258.

[11] Smallwood, A. G., P. S. Thomas, and A. S. Ray. "Characterization of sedimentary opals by Fourier transforms Raman spectroscopy."*Spectrochimica Acta Part-A: Molecular and Biomolecular Spectroscopy* 53, no. 13 (1997): 2341- 2345.

[12]. Fedotova, Maria. "Diamonds as the Alternative Assets on Financial Markets." Master' thesis, 2014.

[13]. Tsunekawa, S., Yu A. Barnakov, V. V. Poborchii, S. M. Samoilovich, A. Kasuya, and Y. Nishina. "Characterization of precious opals: AFM and SEM observations,photonic band gap, and incorporation of CdS nano-particles." *Micro porous materials* 8, no. 5 (1997): 275-282.

[14]. Stewart, A. M., Lewis T. Chadderton, and Brian R. Senior. "Self-assembly in the growth of precious opal." *Journal of Crystal Growth* 312, no. 3 (2010): 391-396.

[15]. Thongnopkun, Pimthong, and Sukanya Pramol."Synthesis and characterization common opal " 37th Congress on Science and Technology of Thailand.

[16]. https://www.opalauctions.com/learn/opal-information/opals-of-the-world. (Accessed on Monday, April 04, 2017, 4:12:47 AM).

[17]. Horton, D."Australian sedimentary opal: why is Australia unique?"*The Australian Gemologist* 21, no. 8 (2002).

[18] https://www.google.com/#q=solid+opal (Accessed on Friday, April 21, 2017, 12:35:21 PM).

[19]. Seid, Ali. "Origin Of opal Hosted in Volcanic Rocks at Koste–Amba and Gift Mariyam, North Shoa (Central–Eastern Ethiopia)." PhD diss., AAU, 2006.

[20]. Pewkliang, Benjamath, Allan Pring, and Joël Brugger. "The formation of precious opal: clues from the opalization of bone." *The Canadian Mineralogist* 46, no. 1 (2008): 139 - 149.

[21]. Shigley, James E."A review of current challenges for the identification of gemstones." *Geologies* 50, no. 4 (2008): 227-236.

[22]. Hatipoğlu, Murat. "Moganite and quartz inclusions in the nano-structured Anatolian fire opals from Turkey." *Journal of African Earth Sciences* 54, no. 1 (2009): 1-21.

[23]. Rondeau, Benjamin, Emmanuel Fritsch, Michel Guiraud, and Christophe Renac. "Opals from Slovakia (“Hungarian” opals)." *European Journal of Mineralogy* 16, no. 5 (2004): 789-799.

[24]. Sodo, A., A. Casanova Municchia, S. Barucca, F. Bellatreccia, G. Della Ventura, F. Butini, and M. A. Ricci. "Raman, FT-IR and XRD investigation of natural opals." *Journal of Raman Spectroscopy* 47, no. 12 (2016): 1444-1451.

[25]. https://en. .wikipedi. webmineral.com, Opal [accessed, 8:12, 1/4/2009 E.c].

[26]. Schumann, Walter. *Gemstones of the World*. Sterling Publishing Company, Inc., 2009.

[27]. Caucia, Franca, Luigi Marinoni, Valentina Bordoni, Christian Ghisoli, and Ilaria Adamo. "Physical and chemical properties of some Italian opals." *Periodico di Mineralogia* 81, no. 1 (2012).

[28]. Starcke, Steven F., Ronald H. Kearnes, Keven E. Bennet, and David A. Edmonson. Method of improving the color of transparent materials." U.S. Patent 5,853,826, issued December 29, 1998.

[29]. Simoni, Martina, Franca Caucia, Ilaria Adamo, and Pietro Galinetto."New Occurrence of Fire Opal from Bemia, Madagascar." *Gems & Gemology* 46, no. 2 (2010).

[30]. https://www.google.com.et/?gws_rd=cr,ssl&ei=YbFfWOP0AcO8acbrvzA#q U sees +and+application+of+opal+gemstone+pdf [accessed at 9:20, 24/12/2016 G.C]

[31]. Choudhary, Gagan, and Rajneesh Bhandari. "A new type of synthetic fire opal: Mexifire."*Gems & Gemology* 44, no. 3 (2008):228-233.

[32]. Yager, T.R. The Mineral Industry of Ethiopia. U.S. Geological Survey Minerals Year Book 2007. Ethiopia [Advance Release]. (2009).

[33]. Hunter, Charles Eric, and Dirk Verbiest. "Silicon carbide gemstones." U.S.Patent 5,723,391, issued March 3, 1998.

[34] Gaillou, Eloïse, Aurélien Delaunay, Benjamin Rondeau, Martine Bouhnik-le-Coz, Emmanuel Fritsch, Guy Cornen, and Christophe Monnier. "The geochemistry of gem opals as evidence of their origin." *Ore Geology Reviews* 34, no. 1 (2008): 113-126.

[35]. Caucia, Franca, Luigi Marinoni, Christian Ghisoli, and Alberto Leone. "Gemological, physical and chemical properties of prase opals from Hanety Hill (Tanzania)." *PERIODICO DI MINERALOGIA* 85, no. 1 (2016): 41-50.

[36]. Valente, Kevin A., Ernest R. Reuter, and Randall M. Wagner. "Device for measuring characteristics of a gemstone." U.S. Patent 5,615,005, issued March 25, 1997.

[37]. Hatipoglu, Murat, Yasar Kibici, Gursel Yanik, Cafer Ozkul, Mehmet Demirbilek, and Yasemin Yardimci."Nano-structure of the Cristobalite and Tridymite Stacking Sequences in the Common Purple Opal from the Gevrekseydi Deposit, Seyitömer-Kütahya, Turkey" 31, No. 1 (2015): 35-49.

[38]. Hatipog, M., N. Can and T. Karali. "Effects of heating on fire opal and diaspore from Turkey." *Physica B: Condensed Matter* 405, no. 7 (2010): 1729-1736.

[39]. Guthrie, George D., David L. Dish, and Robert C. Reynolds. "Modeling the-diffraction pattern of opal-CT." *American Mineralogist* 80, no.7-8 (1995): 869-872.

[40]. Wilson, M. J. "The structure of opal-CT revisited."*Journal of Non Crystalline Solids* 405 (2014): 68-75.

[41]. Caucia, Franca, Luigi Marinoni, Alberto Leone, and Ilaria Adamo. "Investigation on the gemological, physical and compositional properties of some opals from Slovakia ("Hungarian" opals)." *Periodico di Mineralogia* 82, no. 2 (2013): 251-261.

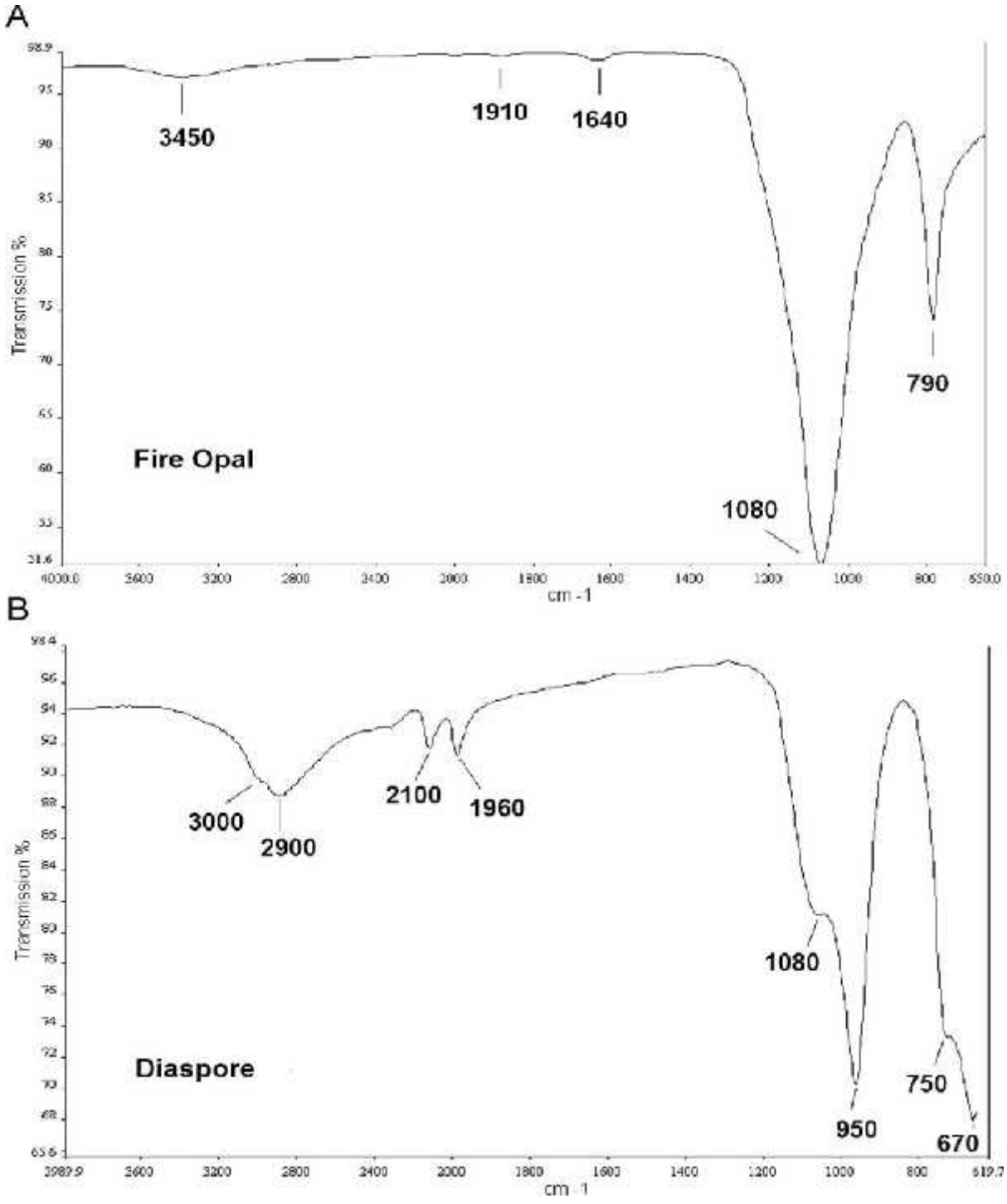
[42]. Makreski, Petre, Gligor Jovanovski, Trajče Stafilov, and Blazo Boev. "Minerals from Macedonia XII. The dependence of quartz and oral color on trace element composition-AAS, FT IR and MICRO-RAMAN spectroscopy study." *Bulletin of the Chemists and Technologists of Macedonia* 23, no. 2 (2004):171-1

[43]. From © *2010 International Centre for Diffraction Data.* [DOI: 10.1154/1.3478554].

[44]. Hatipoğlu, Murat. "The nano-grain sizes of the opaline matrix components in Anatolian fire opals." *Journal of Non-Crystalline Solids* 356, no. 28 (2010): 1408-1415.

8. APPENDICES

Appendix A. FT-IR Spectra of different opal samples from different countries from different literatures.



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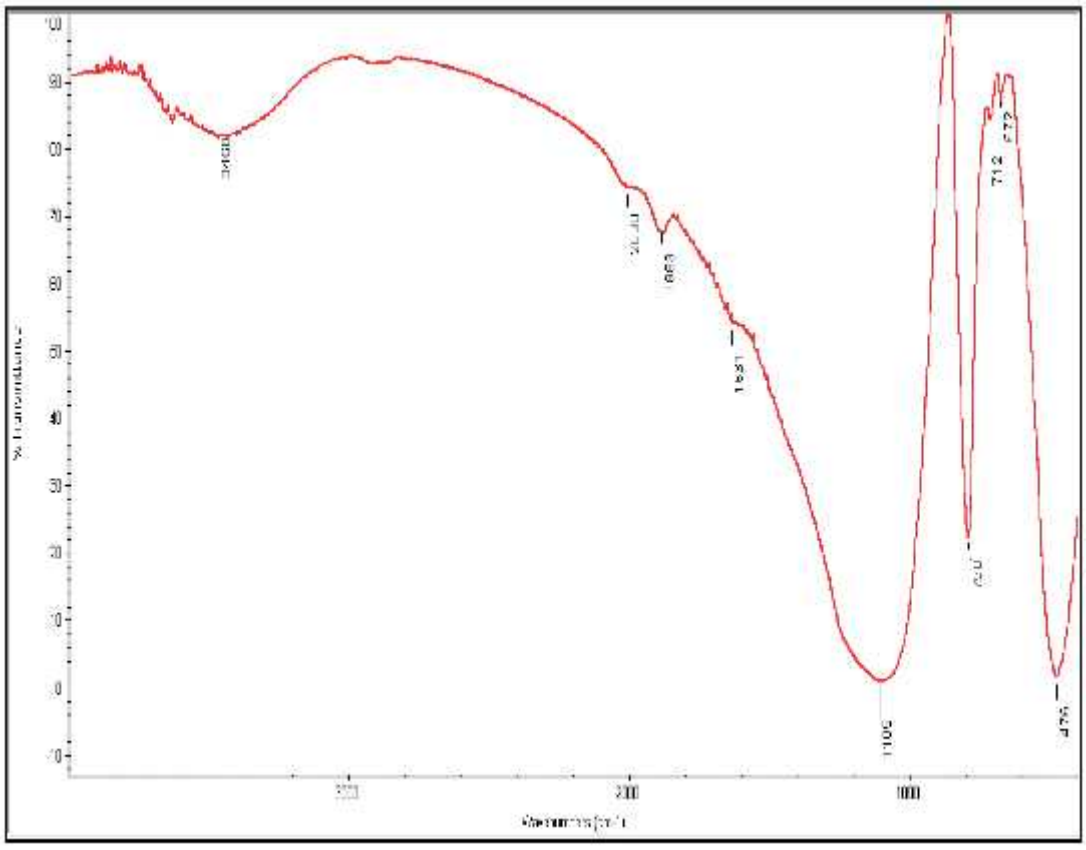

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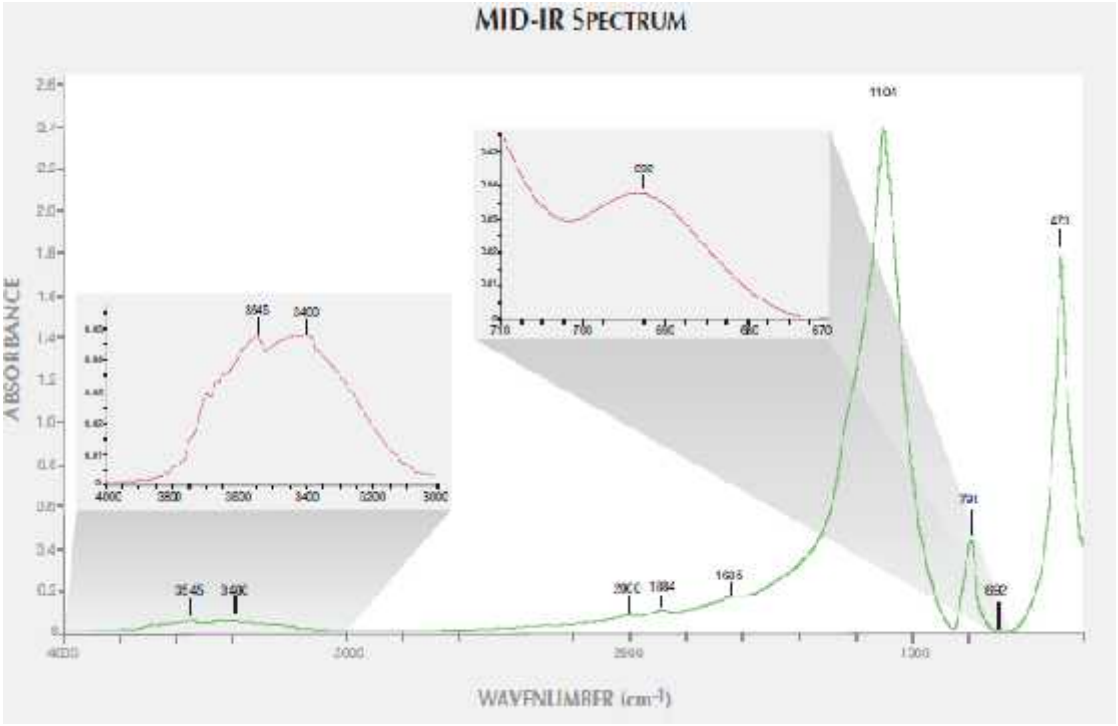
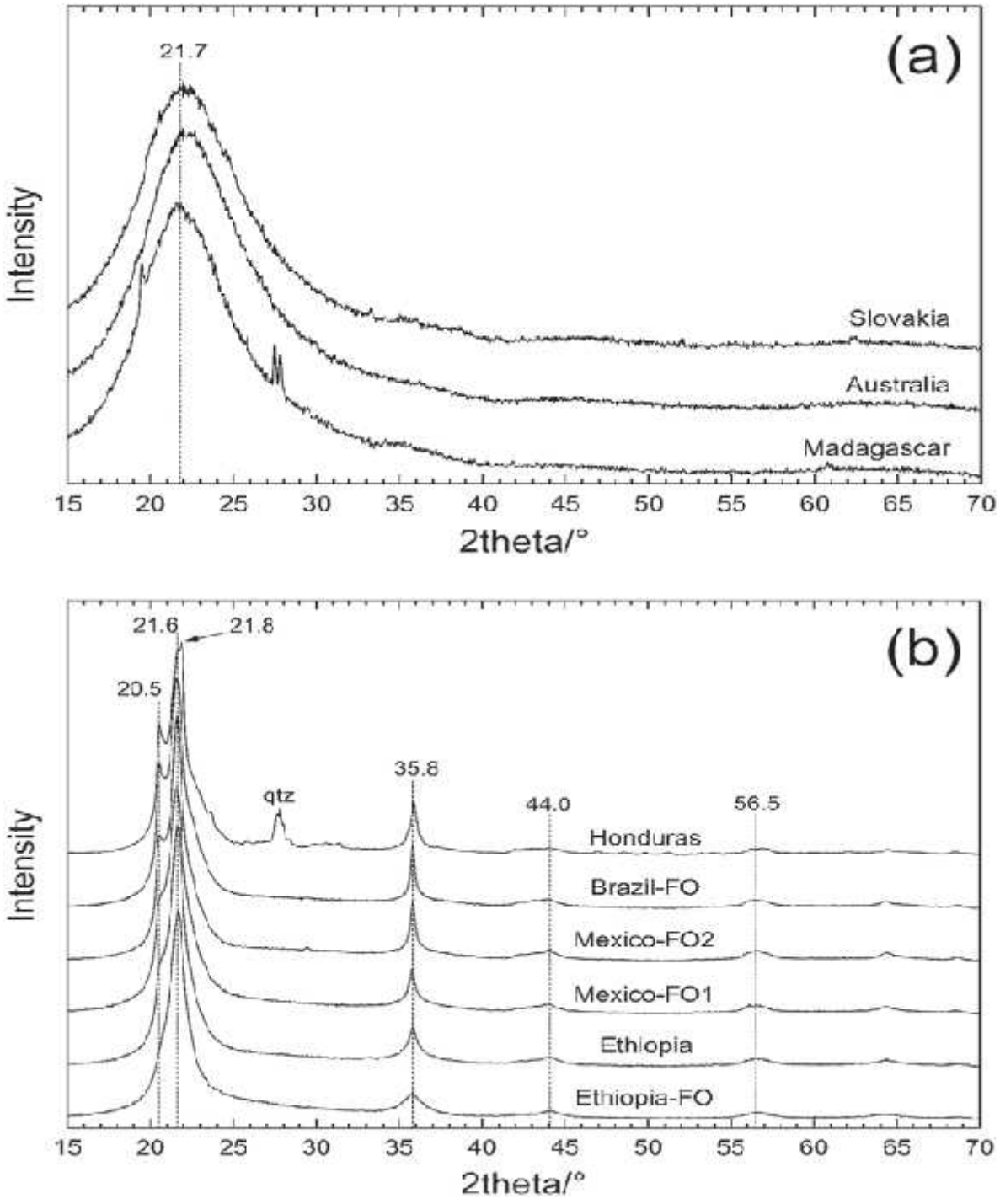

MID-IR SPECTRUM
ABSORBANCE
WAVENUMBER (cm-1)
3545
3400
1101
671

[29]

Appendix B. XRD patterns of different opal samples from different countries from different literatures.



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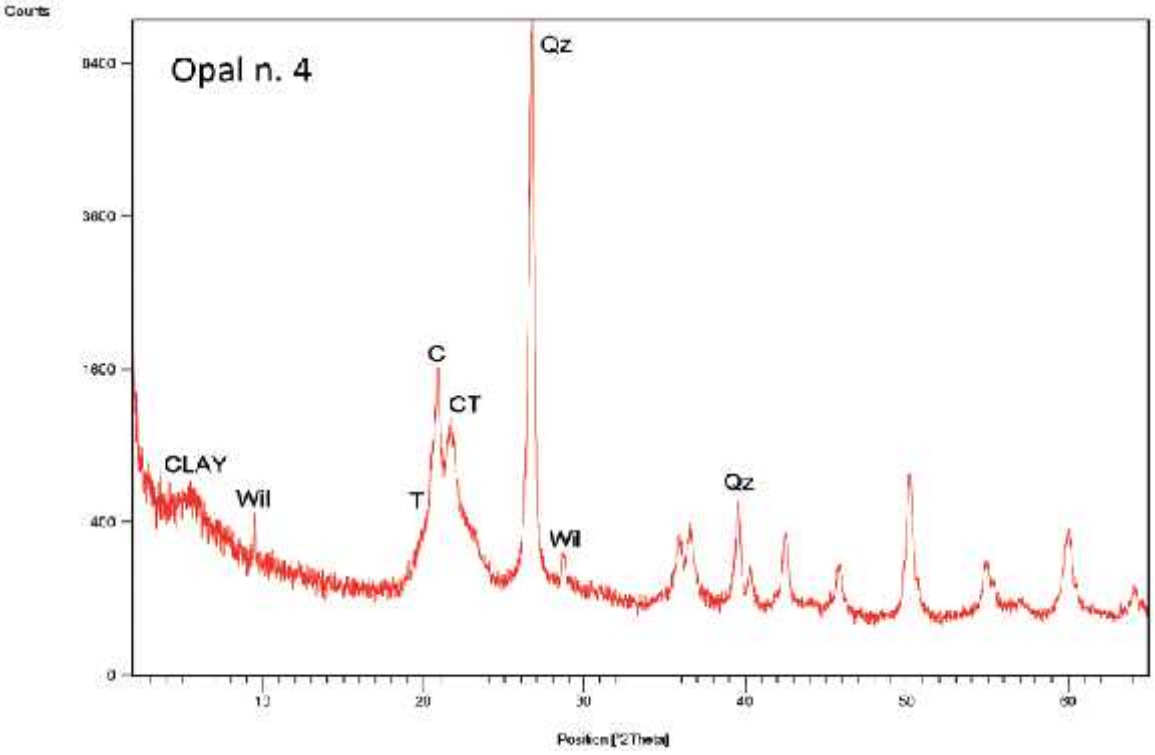
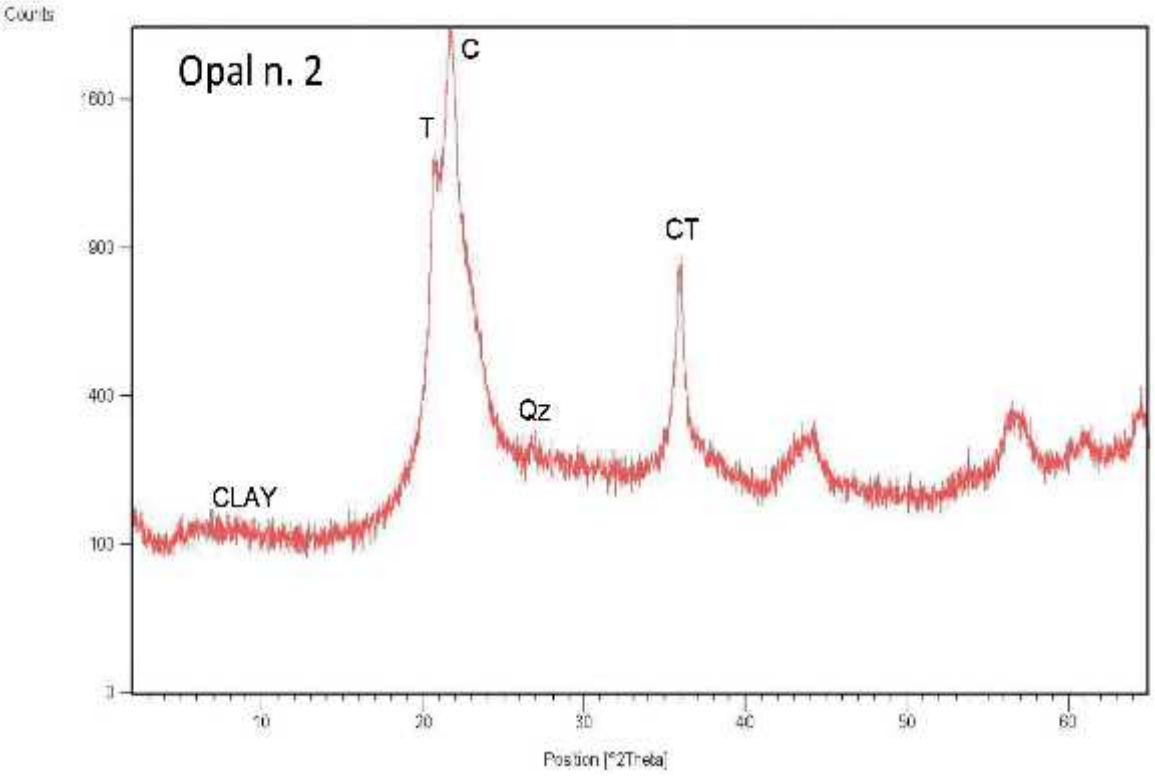
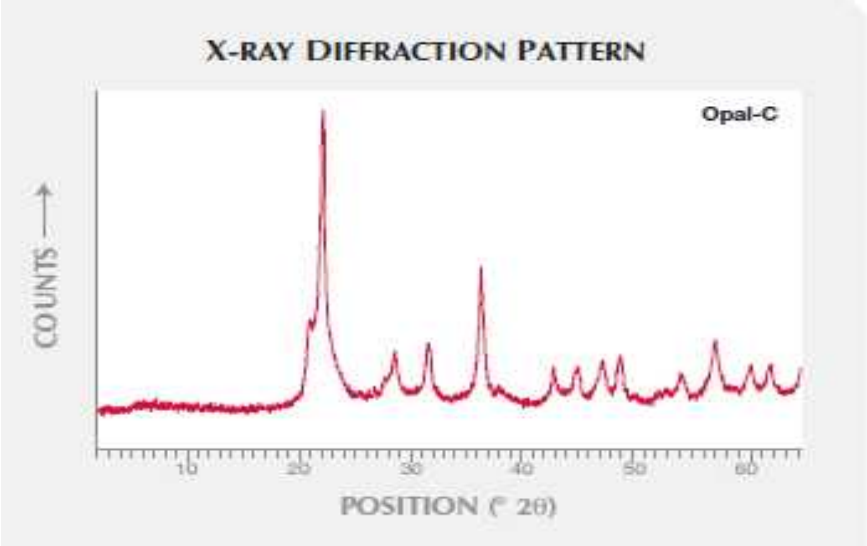
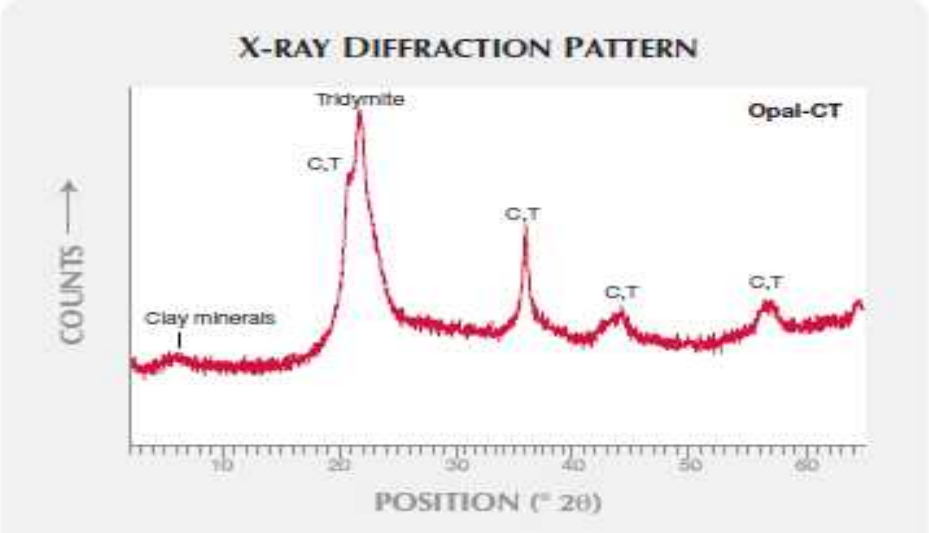

Counts
Opal n. 4
Qz
C
CT
CLAY
Wil
T
Wil
Qz
Position [°2Theta]


Counts
Opal n. 2
C
T
CT
Qz
CLAY
Position [°2Theta]

[35]


X-RAY DIFFRACTION PATTERN
Opal-C
COUNTS
10
20
30
40
50
60
POSITION (° 2θ)


X-RAY DIFFRACTION PATTERN
Tridymite
Opal-CT
C,T
C,T
C,T
C,T
Clay minerals
COUNTS
10
20
30
40
50
60
POSITION (° 2θ)

[29]